THE THEORETICAL ANALYSIS OF GALVANIC CORROSION (Zn, Fe and Cu) UNDER ACTIVATION CONTROL

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by

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(B. Sc. In Chemical Engineering 2004)

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ABSTRACT

For the increasing importance of corrosion in all branches of recent life, a study on behavior of widely industrial metals (zinc, iron and copper) in deaerated hydrochloric acid is presented in this thesis.

This work was developed to predict the corrosion rate and corrosion potentials of binary and ternary metal system to investigate and discuss the effect of temperature, concentration and area fraction of metals on the corrosion rate and corrosion potential.

Metals used were iron, copper and zinc. First the corrosion of these metals was theoretically studied and compared with experimental work and then the same analysis is held down the present study to explain the free corrosion of each metal, galvanic coupling and ternary galvanic system of these metals.

The analysis were performed for pH=0.7, temperatures of 30, 45 and 60^{o}C and for area ratios of 0.5, 1 and 2 for comparison with experimental work. The other analyses were for pH range of 1-3, temperature range of 20-60 and various area fractions of the used metals.

It was found that the calculated results is close to experimental results, and the galvanic coupling increases the corrosion rate of the anodic (active) metal over that if it was under free corrosion condition, and the ternary system has the highest corrosion current.

In all conditions the trend of calculated results is as follows: an increase in temperature increases the corrosion current but decreases the corrosion potential

at constant pH value. Increasing pH increases the corrosion potential but decrease the corrosion current when fixing temperature.

The area fraction had a noticeable effect on the galvanic corrosion rate and galvanic corrosion potential where as the area fraction of more noble metal increases the corrosion potential increases and the corrosion current increases.

In ternary galvanic system, zinc had act as a sacrificial anode and protect iron and copper which act as a cathode.

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Nomenclature

a_{oxd}	Activity of oxidized reagent
a_{red}	Activity of reduced reagent
C_s	Surface concentration (M)
$C_s^{\backslash}$	Deviated surface concentration (M)
E	Potential (V)
E^o	Standard electrode potential
E^a	Anodic potential
E^{eq}	Equilibrium potential
E^c	Cathodic potential
E^{corr}	Corrosion potential
E^{couple}	Coupling potential
e^-	electron
emf	Electromotive force (V)
f	Area fraction (area of one metal / total area of metals)
F	Faraday's number (96487 coulombs/equivalent)
H^+	Hydrogen ion
H_2	Hydrogen gas
i	Current density (µA/cm^2)
I	Current (µA)
i_o	Exchange current density (µA/cm^2)
$i_o^{\backslash}$	deviated exchange current density (µA/cm^2)
i_a	Anodic current density (µA/cm^2)
i_c	Cathodic current density (µA/cm^2)
$i_{o,a}$	Anodic exchange current density (µA/cm^2)
$i_{o,c}$	Cathodic exchange current density (µA/cm^2)
$i_{o,H}$	Exchange current density for hydrogen evolution on metal
$i_{o,T}$	Exchange current density (µA/cm^2) at T
$i_{o,298}$	Exchange current density (µA/cm^2) at 298K
I_{zn}	Anodic current of zinc electrode(µA)
I_{cu}	Anodic current of copper electrode(µA)
I_{fe}	Anodic current of iron electrode(µA)
I_{czn}	Cathodic current of zinc electrode(µA)
I_{ccu}	Cathodic current of copper electrode(µA)
I_{cfe}	Cathodic current of iron electrode(µA)
n	Number of electrons
O^{-2}	Oxygen ion
pH	Hydrogen activity

R	Gas constant (3.814 J/(K.mol))
R_f	Resistance produced by films
R_{soln}	Electrical resistance of solution
α	Symmetry factor
α_a	Anodic symmetry factor
α_c	Cathodic symmetry factor
η	Polarization
η_R	Resistance polarization
ν	Stoichiometric factor

Abbreviations

AES	Auger electron spectroscopy
EDDS	Ethylenediaminedisuccinic acid
emf	Electromotive force
HAZ	Heat affect zone
Ppm	Part per million
SEM	Scanning electron spectroscopy
XPS	X- ray photoelectron spectroscopy

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CHAPTER ONE

Introduction

1.1 Preliminary

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment [1], by other means is the interaction of a metal with its surroundings [2]. The metal ceases to be an element and becomes a compound [3]. Pure metals and alloys tend to enter into chemical union with the elements of a corrosive medium to form stable compounds similar to those found in nature [4].

Deterioration by physical causes is not called corrosion, but is described as: erosion, galling, or wear. In some instances, chemical attack accompanies physical deterioration as described by the terms: corrosion erosion, corrosive wear, or fretting corrosion [1].

The degradation of plastics, concrete, wood and other non-metallic materials which are susceptible to swelling, crazing, softening, etc. is physiochemical rather than electrochemical in nature [4].

“Rusting” applies to the corrosion of iron or iron-base alloys with the formation of corrosion products consisting largely of hydrous ferric oxides. Non-ferrous metals; therefore, corrode but do not rust [1].

Galvanic corrosion occurs when dissimilar metals are in contact in the presence of an electrolyte [4, 5, 6 and 7]. Electrolytes are electrically conductive solutions produced when atmospheric condensation, precipitation or moisture, other sources is contaminated with salts, acids, or alkalis [6].

The galvanic corrosion is stimulated by the potential difference that exist between the two metals, the more noble metal acting as a cathode where some oxidizing species is reduced, the more active metal which corrodes acting as the anode [8]. However the greater the mass of cathodic material relative to the anodic material, the greater the amount and rate of galvanic corrosion and vice versa [9].

1.2 Corrosion Importance

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, and so on [1]. Recent studies on multi-metallic galvanic couples of high strength materials in aggressive environments declared that the number of failures in bridges and other equipments could be reduced [7].

The second area is improved safety of operating equipment which; through corrosion, may fail with catastrophic consequences. Examples are pressure vessels, boilers, metallic containers for toxic materials, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms [1].

Third is conservation, applied primarily to metal resources-the world's of these is limited, and the wastage of them includes corresponding loses of energy and water reserves associated with the production and fabrication of metal structures. Not least important is the accompanying conservation of human effort entering the design and rebuilding of corroded metal equipment, otherwise available for socially useful purposes [1].

The extensionally used parts in the recent life are periodically wear out and break down, much of that is due to corrosion. Annually, a tremendous amount of money is lost in corrosion in the United States. Figures change each year, but a reasonable estimate for the year 2006 is 400 billion $ [6].

1.3 Corrosion Principles

The overall corrosion reaction consists of two separate reactions:
a) an oxidation reaction
b) a reduction reaction.

The above two reactions occurring simultaneously at discrete points on the metallic surfaces. The flow of the electricity from the anodic to the cathodic areas may be generated by local cells set up on a single metal (because of local point to point differences on the surface) or between dissimilar metals [4].

Thus, the electrochemical reaction leads to the production or elimination of ions or electrons, the driving force then becomes the electrochemical free energy [10].

The more important factors involved corrosion phenomena may be summarized as follows:

1- Metal: composition, detailed atomic structure, microscopic and macroscopic heterogeneities, stress (tensile, compressive, cyclic) etc.

2- Environment: chemical nature, concentrations of reactive species and deleterious impurities, pressure, temperature, velocity, impingement, etc.

3- Metal – Environment interface: kinetics of metal oxidation and dissolution, kinetics of reduction species in solution, nature and location of corrosion products [11].

An oxidation or anodic reaction is indicated by an increase in valence or a production of electrons. A decrease in valence charge or the consumption of electrons signifies a reduction or cathodic reaction [12].

1.4 Corrosion Forms

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by visual observation. The corrosion forms are: uniform attack, crevice corrosion, pitting, intergranular corrosion, selective leaching or parting, erosion corrosion, stress corrosion cracking, and galvanic corrosion [13].

1.5 Aim of the Work

This work was developed to predict the corrosion rate and corrosion potentials of binary and ternary metal system to investigate and discuss the effect of temperature, concentration and area fraction of the metals zinc, iron and copper on the corrosion rate and corrosion potential.

CHAPTER TWO
CORROSION

2.1 Corrosion

As mentioned in the previous chapter, corrosion is the electrochemical interaction of a metal with its surrounding so metallic corrosion is the result of a basic chemical reaction which can be separated into two or more partial reactions. These partial reactions are divided into two classes: oxidation and reduction [2].

Oxidation is the loss of electrons. This can be illustrated by the reaction of a metal m to produce a metallic ion [2].

$$m \leftrightarrow m^{+n} + ne^{-} \qquad \text{….. (2.1)}$$

For every oxidation there must be a corresponding reaction involving the gain of electrons, this is reduction reaction. The discharge of hydrogen gas is typical example of such a reaction [2].

$$2H^{+} + 2e^{-} \longleftrightarrow H_{2} \qquad \text{….. (2.2)}$$

The above two simultaneous half reactions are the basis for an electron half cell. So the oxidation at anode (loss of electrons) and reduction at the cathode (gain of electrons). Electricity is generated due to electric potential difference between two electrodes. This potential difference is created as a result of the difference between individual potentials of the two electrodes with respect to the electrolyte. The standard electrode potential is the measure of the individual potential of any electrode at standard ambient conditions (temperature 298 k, solutes at 1M and gases at 1 bar). In most cases, real cells is operated under non – standard conditions. Given the standard cell potential, the non – standard cell potential can be calculated using the Nernest equation [14].

$$E^{eq} = E^{o} - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxd}} \qquad \text{..... (2.3)}$$

2.2 Factors Influencing Corrosion:

2.2.1 pH of Solution:

The corrosion rate of most metals is affected by pH the relationship tends to follow one of three patterns:

1- Acid soluble metal such as iron has a relationship as shown in fig 2.1. In the middle pH range (4 to 10) the corrosion rate of transport oxidizer (usually dissolved O_2) at the metal surface. At very high temperatures such as those encountered in boilers, the corrosion rate increases with increasing basicity as shown by the dashed line [4].

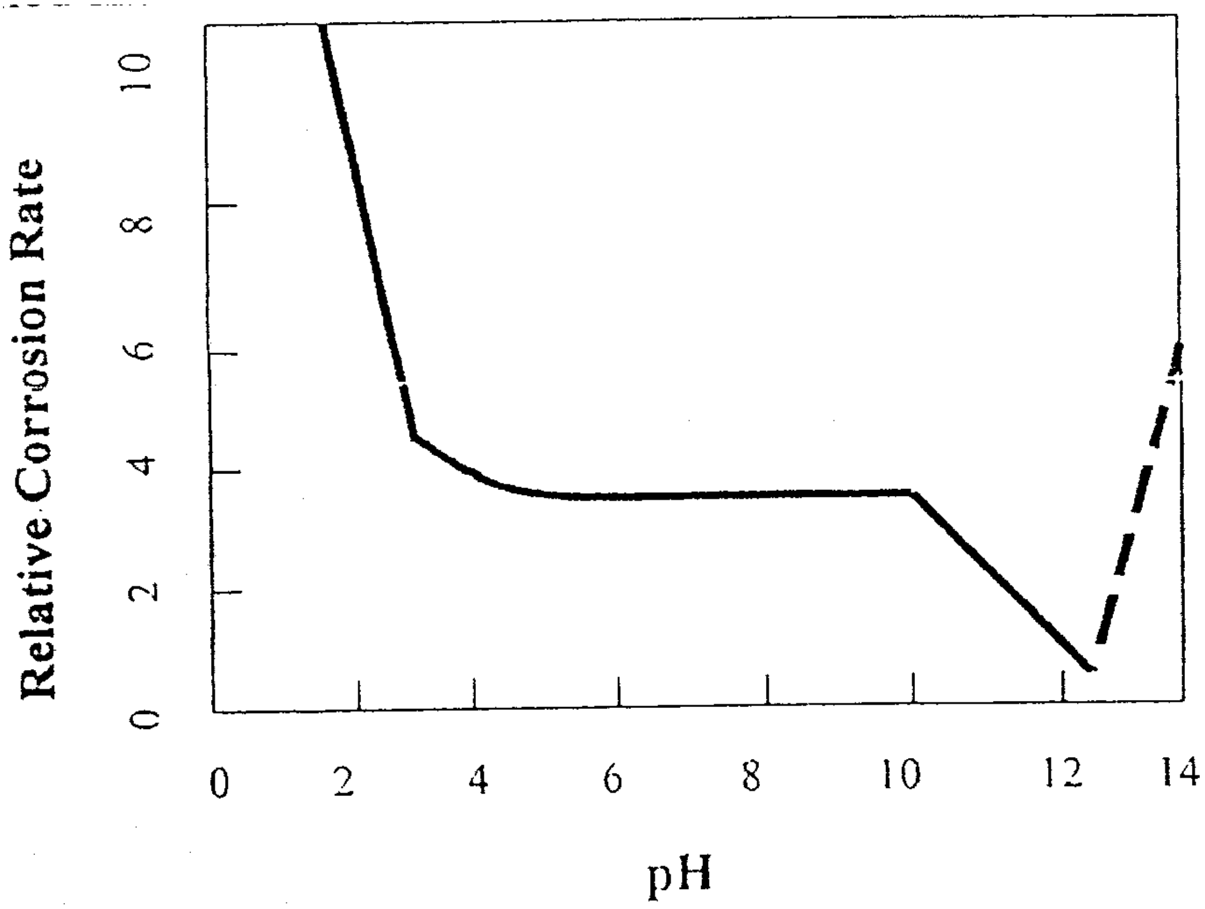

Figure 2.1 effect of pH on corrosion rate of acid soluble metal [4]

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

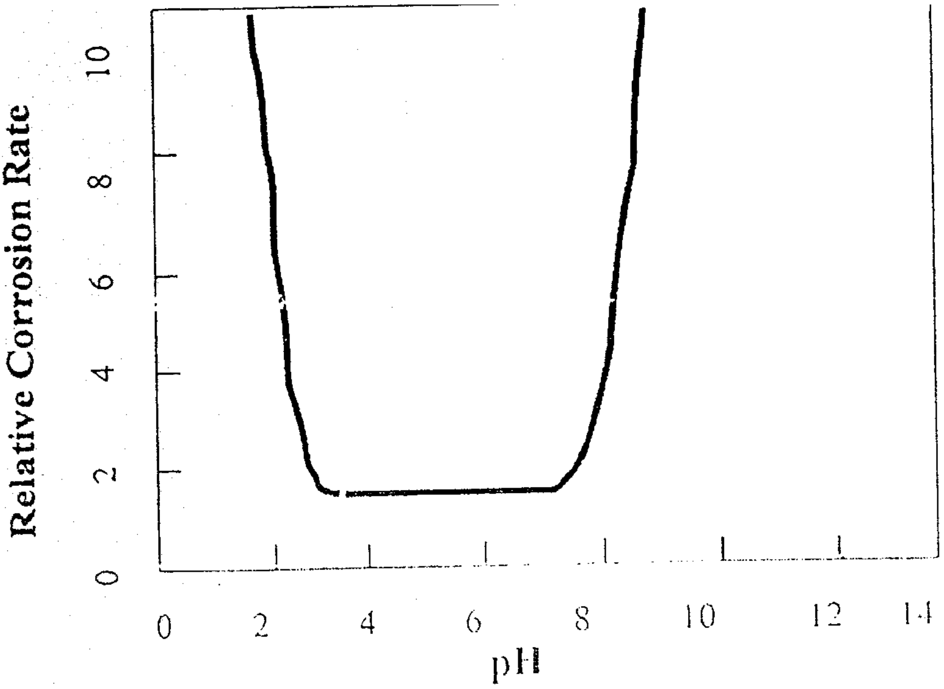

Figure 2.2 Effect of pH on the corrosion rate of amphoteric metals [4]

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

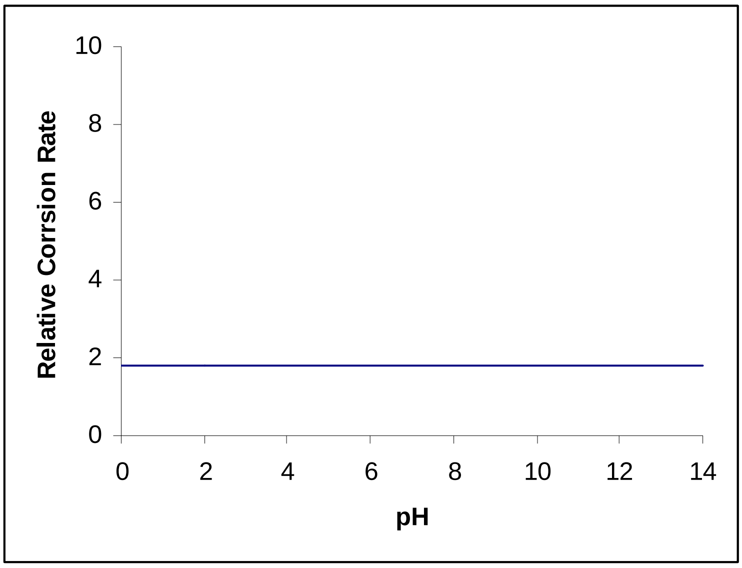

Figure 2.3 Effect of pH on the corrosion rate of noble metal [4]

2.2.2 Oxidizing agents

In some corrosion processes, such as the solution of zinc ions in hydrochloric acid, hydrogen must evolve as a gas. In others, such as relatively low concentration of copper in sodium chloride, the removal of hydrogen, which must occur so that corrosion may proceed is affected by a reaction between hydrogen and some oxidizing chemical such as oxygen to form water. Oxidizing agents are often powerful accelerators of corrosion process, and in many cases the oxidizing power of a solution is its most important single property in so far as corrosion is concerned.

Oxidizing agents that accelerate the corrosion of some materials may also retard corrosion of others through the formation on their surface of oxide layers of absorbed oxygen which make them more resistant to chemical attack. This property of chromium is responsible for the principal corrosion – resisting characteristics of the stainless steel [4].

2.2.3 Temperature

The rate of corrosion tends to increase with rising temperature. Temperature also has a secondary effect through its influence on the most common oxidizing substance influencing corrosion. In addition temperature has specific effects when a temperature charge causes phase changes which introduce a corrosive second phase. Examples include condensation system and systems involving organics saturated with water [4].

2.2.4 Velocity

An increase in the velocity of relative movement between a corrosive solution and a metallic surface frequently tends to accelerate corrosion. This effect is due to higher rate at which the corrosive chemicals including oxidizing substances (air), are brought to the corroding surface and to the higher rate at which corrosion products**,** which might otherwise accumulate and stifle corrosion, are carried away . The higher the velocity, the thinner will be the films which corroding substances must penetrate and through which soluble corrosion products must diffuse [4].

2.2.5 Films

Once corrosion has started, its further progress is very often controlled by the nature of films, such as passive films that may form or accumulate on the metallic surface. The classical example is the thin oxide film that forms on stainless steels.

Insoluble corrosion products may be completely impervious to the corroding liquid and; therefore, completely protective or they may be quite permeable and allow local or general corrosion to proceed unhindered. Films that are non-uniform or discontinuous may tend to localize corrosion in particular areas or to induce accelerated corrosion at certain points by initiating electrolytic effects of the concentration – cell type. Films may tend to retain or absorb moisture and thus, by delaying the time of drying, increase the extent of corrosion resulting from exposure to the atmosphere or to corrosive vapor.

It is agreed generally that the characteristics of the oxide films that form on steels determine their resistance to atmospheric corrosion. The rust films that form on low – alloy steels are more protective than those form on unalloyed steel [4].

2.2.6 Invironment's Impurities

Impurities in a corrodent can be good or bad from a corrosion stand point. An impurity in a stream may act as inhibitor and actually retard corrosion. However, if this impurity is removed by some process change or improvement, a marked rise in corrosion rates can be resulted. Other impurities; of course, can have very deleterious effects on materials. The chloride ion is a good example; small amounts of chlorides in a process stream can break down the passive oxide film on stainless steels [4].

2.2.7 Other Effects

Stream concentration can have important effects on corrosion rates. Unfortunately, corrosion rates remain constant with time over wide ranges, others slow down with time and some alloys have increased corrosion rates with respect to time. Situations in which the corrosion rate follows a combination of these paths can develop. Therefore; extrapolation of corrosion data and corrosion rates should be done utmost caution [4].

2.3 Polarization

Often misnamed (over potential). Polarization is the difference between electrode potential (when it is not in equilibrium with its environment) with respect to the standard electrode potential, the symbol commonly used is η. Polarization can be conveniently divided into three different types [13].

2.3.1 Activation polarization

Activation polarization refers to an electrochemical process which is controlled by the reaction sequence at the metal – electrolyte interface. This is easily illustrated by considering hydrogen – evolution reaction on metal during corrosion in acid solution [13].

2.3.2 Concentration polarization

Also named (diffusion) or (transport) polarization. This type refers to electrochemical reactions which are controlled by the diffusion in the electrolyte. The concentration of hydrogen ions in solution are quite small and the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface. Note that in this case the reduction rate is controlled by process occurring within the bulk solution rather than at the metal surface [13].

2.3.3 Resistance polarization

In corrosion process the resistance of the metallic path for charge transfer is negligible; resistance polarization is determined by factors associated with the metal surface. This resistance polarization can be defined as:

$$\eta^{R} = R_{so\ln} + R_{f} \qquad \text{...... (2.4)}$$

Where R_{soln} is the electrical resistance of the solution which is dependent on the electrical resestivity of the solution and the geometry of the corroding system, R_f is the resistance produced by films or coating formed on or applied to the surface of the sites the last will completely block contact between the metal and the solution increasing the resistance polarization [11].

2.4 Galvanic Corrosion

When a more noble metal or alloy is in metallic contact with a less noble one, the corrosion rate of the latter is higher and that of the former is lower than when the two materials are separated [15].

In this way the galvanic corrosion will be formed in which spontaneous electrochemical corrosion occurs, oxidation occurs at the more active metal (the anode) and the electrons flow from the anode to the more noble metal (the cathode). Thus the anodic metal corrodes but the cathodic metal may not [6].

2.4.1 Galvanic Corrosion Requirements

The following fundamental requirements have to be met for galvanic corrosion:

1. Dissimilar metals
2. Electrical contact between the dissimilar conducting materials (can be direct contact or a secondary connection such as a common grounding path).
3. Electrolyte in contact with dissimilar conducting materials [16].

2.4.2 Galvanic Series

The role of anode or cathode for a given couple will change as the members of the couple change according to the potentials with respect to one another. The sorting of metals and alloys in a conductive environment is the galvanic series (see appendix G) [17].

2.4.3 Factors Influencing Galvanic Corrosion

The two major factors affecting the severity of galvanic corrosion are:

1. The voltage difference between the metals on the galvanic series (see appendix G)
2. The size of the exposed area of the cathodic metal relating to that of the anodic metal [18].

2.4.4 Theory of Galvanic Corrosion:

The galvanic couple between dissimilar metals can be treated by application of mixed potential theory [19].Consider a galvanic couple between a corroding and an inter 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 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. 2.4

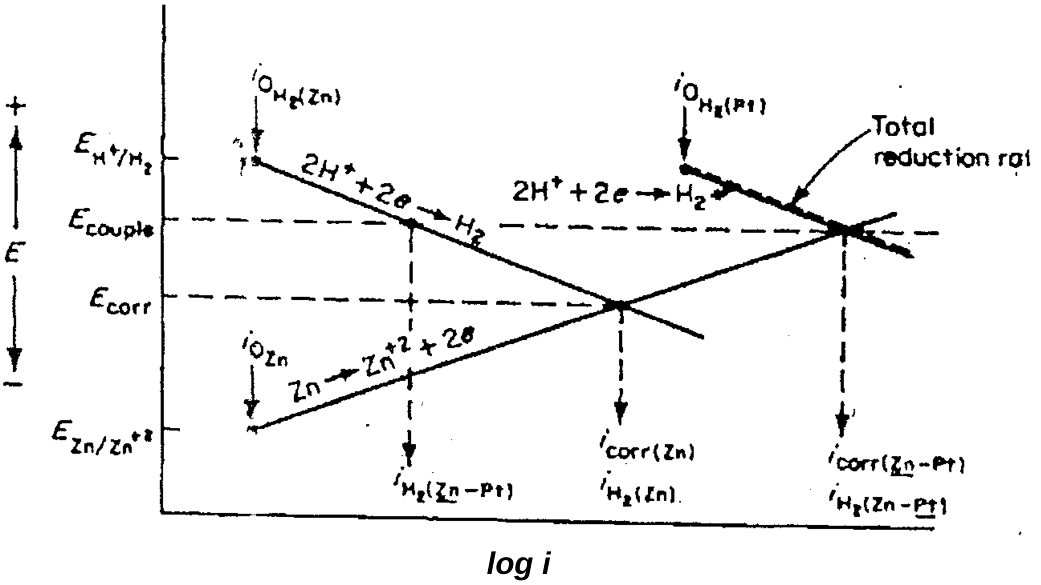

Figure 2.4 effect of galvanically zinc coupled to platinum [19]

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_{corr}(Zn). When equal areas of platinum and zinc are coupled, the total rate of hydrogen evolution is equal to the sum of the rate 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.2.4. Figure 2.4 shows that coupling zinc to platinum shifts the mixed potential from E_{corr} to E_{couple} , increases corrosion rate form i_{corr}(Zn) to i_{corr}(Zn-Pt) and increases the rate of hydrogen evolution on the zinc from I_{H2} (Zn) to I_{H2}(Zn-Pt). The rate of hydrogen ion reduction on the platinum is I_{H2}(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 series (see appendix F) and galvanic series (see appendix G). The reversible potential of the gold electrode is more positive than that of platinum in the emf series, where as in most galvanic series tabulations the position of the platinum below gold .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 [20].

A couple between a corroding and an inter 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. 2.5

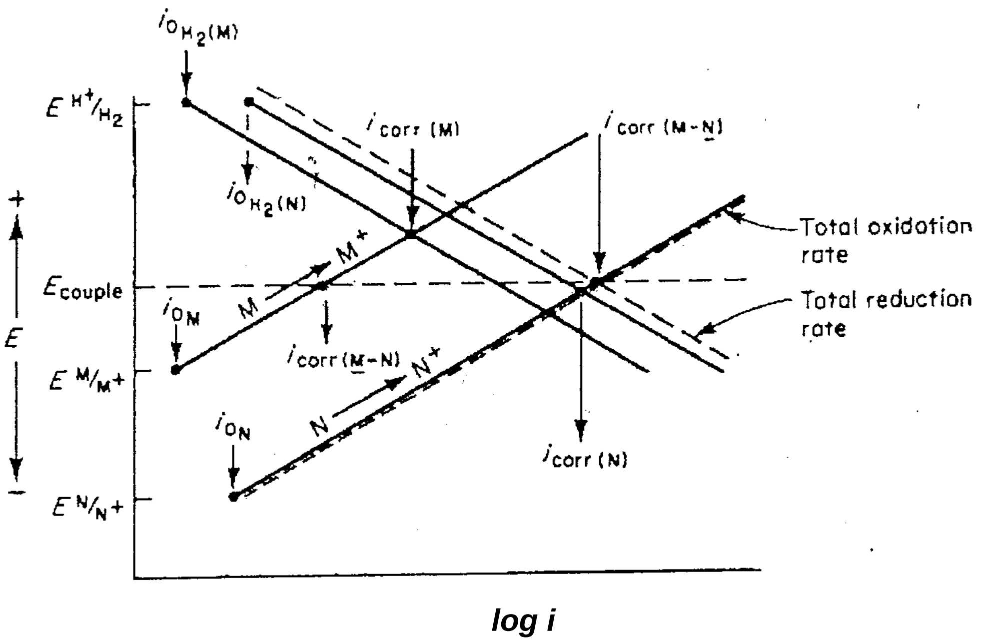

Figure 2.5 galvanic couple between two corroding metal [20]

The fig. 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 couple, the resultant mixed potential of this system occurs at the point where the total oxidation rate equal total reduction rate. The rates of the individual partial processes are determined by the mixed potential. As shown in fig. 2.5 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-$\underline{N}$) [20].

The relative areas of the two electrodes in a galvanic couple also influence galvanic behavior. Fig.2.6 illustrates the effect of cathode area on the behavior of a galvanic couple of zinc and platinum.

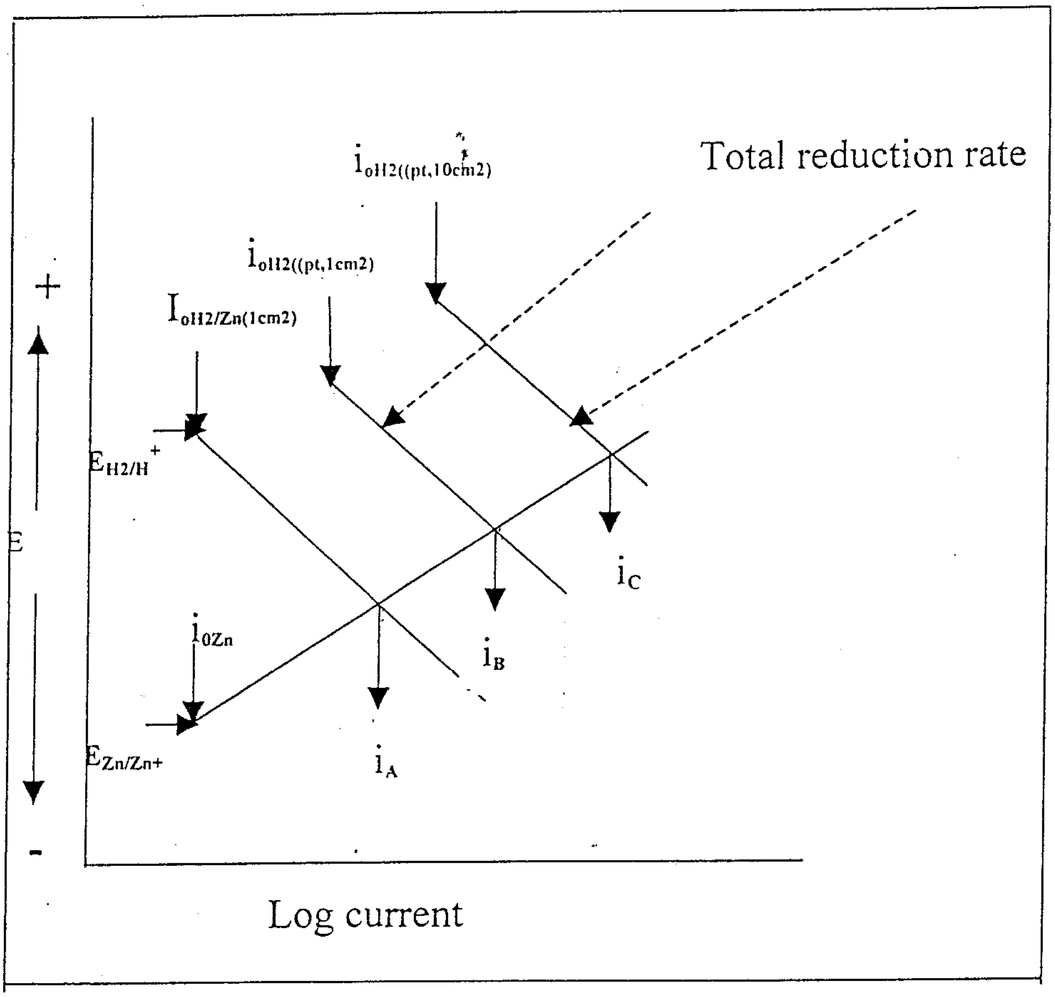

Figure 2.6 effect of cathode-anode ratio on galvanic corrosion of zinc-platinum couple [20]

Current rather than current density is used in this figure. If a piece of zinc 1 cm^2 areas is exposed to the acid solution, it will corrode with a rate equal to i_A.

Note that since 1 cm² of zinc is considered, current and current density i_A are equal. If this zinc specimen is coupled to a platinum electrode of 1 cm² areas, current and current density are equal. However, if a platinum electrode with an area 10 cm² is used and its behavior in terms of current is plotted, it has an exchange current i_o^*, which is 10 times greater than 1cm² 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 fig. 2.6, as shown the corrosion rate of the couple is increased as the area of platinum is increased. As the area of the cathode in a galvanic couple is increased, the corrosion rate of the anode is increased. If the relative area of the anode to the cathode electrode in a galvanic couple is increased, its overall corrosion rate is reduced.

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 S, is made up of fractions f^a, f^b, etc for the various component A, B… then the anodic current from the j^{th} component is:

$$I_a^{system} = \sum_j j_a^j = S \sum_j f^j i_a^j \qquad \text{….. (2.5)}$$

Similarly, the total cathodic current is:

$$I_c^{system} = \sum_j j_c^j = S \sum_j f^j i_c^j \qquad \text{….. (2.6)}$$

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

$$I_{corr}^{system} = I_{a}^{system} = \left| I_{c}^{system} \right| \qquad \text{..... (2.7)}$$

And:

$$\sum f^{j} i_{a}^{j} = \sum_{j} f^{j} \left| i_{c}^{j} \right| \qquad \text{..... (2.8)}$$

Where the current densities on the various component 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 (2.9) [10]:

$$\frac{i_{a}^{B}}{i_{c}^{N}} = \frac{f^{N}}{f^{B}} \left[\frac{\left| i_{c}^{N} \right|}{i_{a}^{N}} - 1 \right] + \left[\frac{\left| i_{c}^{N} \right|}{i_{a}^{N}} \right] \qquad \text{..... (2.9)}$$

For instance [21] if a metal is placed in an 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 it dissolves. Such a spontaneous reaction, called galvanic displacement, continues until the base metal is with a “flash” porous coating of the more noble one, possibly 1μm or so in thickness , where upon further reaction substantially ceases. Iron dipped in to 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 $\frac{|i_c^N|}{i_a^N}$ 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 metal N and a base metal B immersed in a corrodent, the corrosion of the resulting polyelectrode can be represented by equation (2.9) 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 the N (fb<<fn) 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

a. The relative area (fn/fb)and
b. The relative electrochemical activities of the metals concerned.

2.4.5 Literature Review on Galvanic Corrosion:

Luigi Galvani [22] in 1780 discovered that when two different metals (copper and zinc) were connected together and then both touched to different parts of nerve of frog leg at the same time, they made the leg contract. He called this “animal electricity “.

Ericson- Auren et. al. [23] in 1901 showed that the rate at which zinc dissolves in hydrochloric acid of different concentrations is not that required by a plain application of the mass law. It can be accounted for on the hypothesis that the rate was due to local galvanic action.

Copson [24] in 1945 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 .

Stern [25] in 1958 had noted that both Ti and type 316 stainless steel in nitrate – inhibited solutions of ferric and ferrous chloride exhibited positional, which were very close to the reversible ferric – ferrous potential of the solution .An experiment was designed where various area ratios of Ti and type 316 stainless steel could be coupled together to determine the effect of the area fraction on cathodic polarization. It was found that a polarization curve on a surface with regions exhibiting different over – voltage parameters for the same reaction is the sum of the individual polarization curves when plotted on a current basis. Polarization diagrams which introduce the concept of exchange current can be used to show how anode and cathode areas affect corrosion rate and corrosion potential.

Pryor [26] in 1958 investigated the galvanic corrosion of Al / steel couple in chloride ions containing solution and found that aluminum completely protects steel cathodically within the pH range o – 14 and the galvanic current and the corrosion rate of aluminum were at a minimum in the nearly neutral pH range .

Warnglen [27] in 1969 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.

Zanker et al. [28] in 1969 studied the galvanic behavior of the Fe-Cd couple , and the polarity of Cd with respect to Fe in $NaHCO_3$, $NaNO_3$ and NaCl solution at 25°C . Direct coupling as well as contact through a resistor and open – circuit electrode reversal of polarity was observed in $NaHCO_3$ (where it occurred earlier in a more concentrated solution) and in $NaHCO_3$ + $NaNO_3$, but reversal did not occur in pure NaCl or $NaNO_3$. The result were confirmed on commercial Cd – plated Fe the polarity reversal was attributed to the formation of an anodic insulating film on Cd and related to the buffering properties of bicarbonate .

Shalaby [29] in 1971 studied the effect of galvanic coupling of Ti with admiralty brass Al – brass , Cu – Ni and Al – Mg alloys in 32 – 7 g / L NaCl solution at ambient temperature and 90° C under flowing CO_2 and (Ar) atmospheres . The results showed that Ti 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 relatively large area of Ti (1: 10) it showed a pitting corrosion.

Oldham et.al.[30] in 1972 studied the treatment of corrosion of galvanic couples in which the area of one metal greatly exceeds that of the other has been carried out using mixed potential theory. A ruptured metallic coating on a metal substrate was encompassed by the treatment, as was a metal containing inclusions of a second metal as impurity two cases were examined. In the first, exemplified by zinc – plated steel, three reactions were considered: dissolution of the coating and reduction of the oxidizing agent on each metal. In this case, the result of the rupture was often a very marked increase in the corrosion of the coating, leading to an autocatalytic effect; the second case treated an active metal protected by coating of a more noble metal. The following reactions were considered: both a directions of the red ox couple generated by the oxidizing agent, and the dissolution of the substrate .It was demonstrated that in the second case the corrosion rate was maximal at vanishingly small porosities. In both cases, corrosion potential can be used as a measure of porosity.

Mansfeld [31] in 1973 worked on galvanic interaction between active and passive titanium in aqueous CH_3OH – 1N HCl and found that if the area ratio (A^C/A^A) was increased to higher value , the anodic would be polarized to more noble potentials and only an oxidation process (dissolution) will occur .

Mansfeld [32] in 1973 investigated the relationship galvanic current and dissolution rates in aerated 3% NaCl; he found that the galvanic current can not be accurate measure of the dissolution rates, since dissolution rates from the galvanic current were smaller than the true dissolution rates

Mansfeld et. al. [33] in 1975 studied the galvanic corrosion of Al alloys 1100, 2024, 2219, 6061 and 7075 coupled to Cu, stainless steel 3041 Ti – 6A-4V , 4130 steel or Zinc has been in 3.5% NaCl, tap water and distilled using electrochemical and weight loss data . In 3.5% NaCl the galvanic effect decrease in the order Cu > 4130 steel > SS 304 L ~ Ti – 6A – 4V for all alloys coupled to one of these metals , while in tab water and distilled water the ranking was Cu >SS 304 L ~ Ti – 6Al – 4V> 4130 steel . Zinc, although being the anodes in all galvanic couples, can sometimes accelerate corrosion rates of all alloys. Dissolution rates of all alloys coupled to given dissimilar material were higher in 3.5 % NaCl than in tap water and distilled water where they were found to be comparable. In assessing galvanic corrosion behavior of a given Al alloy as a function of environment, one has to consider the effect of the dissimilar metal.

the dissolution rate of Al 6061 is, for example , higher in tap water with Cu as cathode than 3.5 % NaCl with SS304 L or Ti-6Al-4V as cathode .

Mansfeld [34] in 1976 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:

$$Ig = constant + constant\ (\sqrt{V}) \qquad \ldots\ldots (2.10)$$

Mansfeld et. al.[35] in 1975 studied the Al alloys 2024 and 7075 have been electrically coupled to Cu , stainless steel 304L , 4130 steel , Ti – 6Al -4V , Cd or Zn in 3.5% NaCl. Galvanic current and weight loss data have been obtained for area ratios $A^c / A^A = 0.1$, 1 and 10 in 24 hours tests. Experimental result confirm theoretical calculations based on mixed potential theory, according to which the galvanic current density ig^A with respect to the anode was directly proportional to the area ratio : $ig^A = K_1\ A^C / A^A$, while the dissolution rate r_A of the anode was related to the area ratio by $r_A = K_2 (1 + A^C / A^A)$. The galvanic current $I_g = K_1\ A^C$. The galvanic current density i_g^A can be converted into dissolution rates r_A according to:

$$R_A = K_g\, i_g^A\ (1 + A^A/ A^C) \qquad \ldots\ldots (2.11)$$

Pohlman [36] in 1978 studied the corrosion and the electrochemical behavior of Boron / Al composites and found that the galvanic corrosion would be expected between the aluminum bromide itermetallic and the aluminum matrix causing preferential attack of the aluminum.

Glass et. al [37] in 1985 studied the electrochemical behavior of zinc and mild steel in 0.01 M $NaHCO_3$ solution saturated with oxygen containing 1%CO_2 at 65° C. Both zinc and steel spontaneously passivated in this environment with steel passivation occurring much more slowly. This result in the observation of a temporary condition of polarity reversal in the zinc – steel coupled. The zinc corrosion product consisted mainly of basic zinc carbonates and it was suggested that these promoted the rapid passivation of zinc and hence the polarity reversal. This poorly conductive corrosion product also resulted in strongly polarized zinc cathodic kinetics .An active steel – passive steel couple was shown to be more damaging to the active steel area than a zinc – steel couple after reversal

Fangteng et al. [38] in 1988 considered the condition under which the cathode of a galvanic couple would the corroded and an equation have been derived to describe this behavior. Cathode corrosion leads to a decrease in the galvanic current. For a large ratio of surface area of cathode to anode and small free corrosion potential difference between the alloys, it was shown that the galvanic current density through the anode was independent of the surface area ratio. It was also shown to be less than the product of the area ratio and the current density due to oxygen reduction at the cathode.

Morris [39] in 1989 studied galvanic current and potentials which have been calculated on heterogeneous electrode surfaces compared to random configurations of coplanar anodes and cathodes, for the purpose of the investigating system behavior on different electrode geometrics. The electrochemical transport equation was solved in the absence of mass – transfer effects with a three –dimensional application of the finite element method. The galvanic current and potential so calculated were investigated for similarities linking behavior on different electrode geometries. It has been found that for a wide range of system parameters galvanic currents scale with the active perimeter separating anodic and regions on the electrode surface. Moreover, this effect enabled the accurate prediction of galvanic current for an arbitrarily complex electrode surface geometry.

Scully [40] in 1993 investigated the electrochemical behaviors of Pt – Al_2 Cu phase , beta – Al_3 Ta , and , to lesser extent , Al_3 Zr compared to high purity Al in ambient temperature inert buffer solution and , in certain cases , dilute halide solutions : the aim of this work was to develop a better understanding of electrochemical characteristics of these intermetallic phase .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 phase were more positive than that of Al in inert solution ranging form pH 2 to 12. The Al_2Cu phase supported the reduction of water reaction at enhanced rates relative to pure Al due to the presence of metallic CuO in an Al_2O_3 rich oxide but supported oxygen evolution due to a combination of this effect as well as formation of more electrically conductive copper oxides .A similar effect was observed for Al_3Ta and was attributed mainly to the formation of a more conductive mixed oxide containing Ta_2O_3.

Tahara et. Al. [41] in 2000 developed potential measurement with a Kelvin probe to measure the electrode potential in the vicinity of an Fe / Zn couple boundary during galvanic corrosion of galvanized steel sheets under thin films of NaCl aqueous solutions of various concentrations . Using the Kelvin probe , the Zn surface potentials were measured for thin films of 0 - 0.5 % NaCl solution , and the obtained values were approximately -1.1 to -1.2 V (versus Kelvin standard). The Kelvin potential of Fe showed a value close to that of the Zn surface in the vicinity of the Fe / Zn boundary , while at a sufficiently remote area it converged to - 0.7 V . The transition zone existed only on the Fe side. The width of the transition Zone decreased with increasing Film thickness and salt concentration of water layer. The sacrificial effect of Zn reaches farther in NaCl solution films than in pure water because of low resistivity of salt solutions .The potential distribution in the boundary can be well explained by the transmission - line model. In thin film system, the effective galvanic distance of Zn on Fe surface was proportional to $(\delta_f/\rho)^{1/2}$. Where ρ is the specific resistance and δ_f is the thickness of water film covering the galvanic couple.

Munoz et. al [42] in 2003 , studied the analysis of the corrosion of Cu - XNi alloys (X = 10 wt % to 30 wt %) and Cu and Ni metals in commercial lithium bromide (LiBr) heavy brine solutions , with and without additives, using polarization curves. Corrosion rates were determined by the tafel slope method, and inhibitor effects were analyzed in the commercial solution. Critical potentials were calculated at 50 μA and it was observed that the nickel content shifted critical potentials to more positive values. Breakdown potentials were calculated in commercial LiBr solution. Galvanic current and mixed potentials were determined using polarization curves according to the mixed potential theory. The result demonstrated that only under particular conditions of pH and concentration of LiBr solution, alloying with nickel improved corrosion resistance of an alloy. In fact, it was observed that the inhibition effect of commercial LiBr (additive with chromate) was always higher for the copper electrode and lower for the nickel one. Commercial solution shifted open current potentials and critical potentials to more positive values. The galvanic behaviors of the studied alloys did not follow a common and generalized character in function of the metallic components of the materials and LiBr concentrations. It is only possible to generalize that the most reactive mixed potentials and the lowest galvanic current were measured in commercial LiBr solution.

Song et. al [43] in 2004 , investigated the galvanic corrosion of magnesium alloy AZ91 D in contact with zinc , aluminum alloy A380 and 4150 steel . Specially designed test panels were used to measure galvanic currents under salt spray conditions .It was found that the distributions of the galvanic current densities on AZ91D and on the cahtodes were different. An insulating spacer between the AZ91D anode and the cathode could not eliminate galvanic corrosion. Steel was the worst cathode and aluminum the least aggressive to AZ91D. Corrosion products from the anode and cathodes appeared to be able to affect the galvanic corrosion process through a “shortcut" effect.

Al – Mayouf [44] in 2005 studied the galvanic coupling between magnetite and iron in ethylenediaminedisuccinic acid (EDDS) solutions both with and without added iron (ІІ) ions using electrochemical methods. The galvanic coupling accelerated the corrosion of iron due to the small shift in its potential in the anodic direction. At the same time, the potential of the magnetite was cathodically polarized away from the potential range where, the only faradic process – the reductive dissolution of magnetite – took place and resulted in a considerable decrease in its dissolution. Magnetite dissolved faster at the galvanic potential when [EDDS] > [Fe $^{+2}$] whereas iron was affected to a much lesser extent. The ratio between the rates of dissolution of magnetite at the galvanic potential to that at its steady state potential tended to decrease at higher temperatures and at higher EDDS and Fe^{+2} concentrations . The study showed that temperature plays a decisive role in the dissolution of magnetite coupled to iron. To completely remove it from the iron surface, high temperatures should be used. Corrosion inhibitors have to be considered when high losses of the base metal can not be tolerated.

Lee [45] in 2005 presented a numerical analysis of galvanic corrosion of a Zn/Fe interface beneath a thin layer electrolyte. Specifically, a circular defect, where the zinc coating has been removed, was considered. It was assumed that both oxygen reduction and iron oxidation can occur on the Fe surface, while only zinc oxidation occurs on the Zn surface. The importance of electrolyte thickness and conductivity and defect radius was considered. It was assumed that the iron and zinc oxidation rates are described by tafel relationship if the kinetic parameters of the oxidation reactions are known, the cathodic protection of Fe is a function of Wagner number, the ratio of the electrolyte thickness to the defect radius, and the ratio of the radius of the defect to the outer radius of the zinc layer.

Eaves et. al.[46] in 2008 reported an analytical method and results for a chemical's potential for corrosion of metal contacts. Corrosion rates were measured via a chemical cell; the current and potential were measured between two wafers coated with dissimilar metals, submerged in process solvent, strippers and etch solution. Galvanic corrosion was more closely correlated to the current of the galvanic as opposed to the potential in static solvent tests. In addition to the static solvent tests, large current spikes were observed when transitioning from one solvent to another. Based on these results, the fundamental design of the metallization scheme as well as multi – solvent process flows was be optimized to minimize galvanic corrosion and subsequent electrical and visual defects. Visual of defects were observed on metal stacks consisting of metals with high galvanic. Potential, specifically aluminum (anodic), nickel, platinum and gold (cathodic). The corrosion effects were varied to be due to galvanic corrosion versus purely chemically etching the metal layers by solvents. Electrically isolated Al pads were unaffected by process chemistry, while Al pads overlapping with au\ Ni pads showed severe corrosion patterns.

Pujar et. al.[47] in 2008 studied the 304 stainless steel in 6m HNO_3 solution and a precipitated $M_{23}C_6$ in heat affect Zone and high corrosion rates in boiling nitric acid .In this connection a study of possible galvanic corrosion effect at the junction of sensitized HAZ and the adjacent base metal in 304 stainless steel in sulphuric as well as nitric acid , was under taken. The corrosion rates observed in nitric acid medium at room temperature did not show enhanced corrosion rate due to galvanic coupling. The corrosion rates at 60^0C where higher in the same medium based on these results, a drastic rise in corrosion rate and the subsequent failure of the waste vault tank was not expected.

2.5 Experimental Work

Al – Hadithy [48] in 2001 studied the effect of temperature and area ratio of cathode to anode on galvanic corrosion of copper, zinc, iron, stainless steel 304 and brass alloy by using multiple zero resistance ammeter. The corrosion rae of the selected couples is compared with corrosion rate of the same metal when left in single situation by using the weight loss method and the potentiostatic polarization methods. Brass alloy was studied using the potentiostatic polarization and weight loss method only.

Three area ratios (0.5, 1 and 2) and three temperatures (30, 45 and 60 °C) were taken into account for galvanic corrosion experiments in special cell designed for this purpose. The same three temperatures were taken into consideration for the single weight loss and potentiostatic polarization experiments. All the above experiments were performed in dearated 0.2N hydrochloric acid environment.

From the above experiments performance it was found that altering the area ratio and increasing the temperature played an important rule in increasing the galvanic corrosion by galvanic current and dissolution rate. When temperature increased, the aggressiveness of corrosion in single weight loss (dissolution) and potentiostatic experiments.

From the weight loss and polarization experiments for single metal, the arrangement of metals to combat corrosion in the environment of dearated 0.2N hydrochloric acid illustrated as follows:

Cu > Brass > stainless steel 304 > iron > zinc

Chapter Three

Theoretical aspects

3.1 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 potential and corrosion rates using equations derived from electrochemical principles. In this chapter, the expressions of corrosion rate and corrosion potential are declared by equations shown further word.

3.2 Activation control

3.2.1 Equilibrium potential

To determine the potential of a system, in which the reduced oxidized species are not at unit activity, the familiar Nernest equation can be employed [13,17].

$$E^{eq} = E^{o} - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxd}} \qquad \text{..... (3.1)}$$

Or written as:

$$E^{eq} = E^{o} - \frac{2.303RT}{nF} \log \frac{a_{red}}{a_{oxd}} \qquad \text{..... (3.2)}$$

Where E^{eq} is the equilibrium half cell potential, E^{o} is the standard equilibrium half – cell potential , R is the gas constant (8.314 J/K ,mol) ,T is the absolute temperature (n) is the number of electrons transferred is the faraday constant

(96487 coulomb / equiv.) a_{red} and a_{oxid} are activities or (concentrations) of oxidized and reduced species. Hydrogen ion activity is commonly expressed in terms of pH. This is defined as:

$$pH = -\log\left(H^{+}\right) \qquad \text{.....} (3.3)$$

3.2.2 Non Equilibrium Potential:

At non equilibrium state:

$$i = i_o \exp\left[\frac{F\alpha n}{RT}\left(E - E^{eq}\right)\right] \qquad \text{.....} (3.4)$$

In terms of cathodic and anodic's currents:

$$i_a = i_{o,a} \exp\left[\frac{F\alpha_a n}{RT}\left(E^{a} - E^{eq,a}\right)\right] \qquad \text{.....} (3.5)$$

$$i_c = i_{o,c} \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{c} - E^{eq,c}\right)\right] \qquad \text{.....} (3.6)$$

Where the hydrogen evolution controls as cathodic reaction.

Corrosion occurs at:

$$i_a = \left|i_c\right| \qquad \text{.....} (3.7)$$

Also

$$E^{a} = E^{c} = E^{corr} \qquad \text{.....} (3.8)$$

3.3 Exchange Current Density:

The variation of exchange current density with temperature is as follows [49]:

$$i_{o,T} = i_{o,298} \exp\left[\frac{E^{act}}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$ ….. (3.9)

The dependence of exchange current density on the change in medium's concentration is as follows [10]:

$$\log \frac{i_o}{i_o^{\backslash}} = \frac{\alpha}{\nu} \log \frac{C_s}{C_s^{\backslash}}$$ …… (3.10)

Normally: $\frac{\alpha}{\nu} \cong 1$ [10] ….. (3.11)

That leads to: $\frac{i_o}{i_o^{\backslash}} = \frac{C_s}{C_s^{\backslash}}$ ….. (3.12)

3.4 Galvanic corrosion

For activation control [50]:

For two metals:

$$I_{a1} + I_{a2} = |I_{c1}| + |I_{c2}|$$ ….. (3.13)

Or in terms of current densities and areas

$$i_{a1} f_1 + i_{a2} f_2 = |i_{c1} f_2| + |i_{c2} f_2|$$ ….. (3.14)

$$E^{a,1} = E^{a,2} = E^{c,1} = E^{c,2} = E^{corr}$$ ….. (3.15)

$$\alpha_{a,1} = \alpha_{a,2} = \alpha_a$$ ….. (3.16)

$$\alpha_{c,1} = \alpha_{c,2} = \alpha_c$$ ….. (3.17)

$$i_{a1} = i_{o,a1} f_1 \exp\left[\frac{F\alpha_a n}{RT}\left(E^{corr} - E^{eq,a1}\right)\right] \quad \text{…… (3.18)}$$

$$i_{a2} = i_{o,a2} f_2 \exp\left[\frac{F\alpha_a n}{RT}\left(E^{corr} - E^{eq,a2}\right)\right] \quad \text{…… (3.19)}$$

$$i_{c1} = i_{o,c1} f_1 \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{corr} - E^{eq,c1}\right)\right] \quad \text{…… (3.20)}$$

$$i_{c2} = i_{o,c2} f_2 \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{corr} - E^{eq,c2}\right)\right] \quad \text{…… (3.21)}$$

And for ternary system:

$$\sum I_a = \sum I_c \quad \text{….. (3.22)}$$

In terms of current density:

$$i_{a,1} f_1 + i_{a,2} f_2 + i_{a,3} f_3 = \left|i_{c,1} f_1\right| + \left|i_{c,2} f_2\right| + \left|i_{c,3} f_3\right| \quad \text{….. (3.23)}$$

And the potentials are:

$$E^{a,1} = E^{a,2} = E^{a,3} = E^{c,1} = E^{c,2} = E^{c,3} = E^{corr} \quad \text{….. (3.24)}$$

And similar to binary system:

$$i_{a1} = i_{o,a1} f_1 \exp\left[\frac{F\alpha_a n}{RT}\left(E^{corr} - E^{eq,a1}\right)\right] \quad \text{….. (3.25)}$$

$$i_{a2} = i_{o,a2} f_2 \exp\left[\frac{F\alpha_a n}{RT}\left(E^{corr} - E^{eq,a2}\right)\right] \quad \text{….. (3.26)}$$

$$i_{a3} = i_{o,a3} f_3 \exp\left[\frac{F\alpha_a n}{RT}\left(E^{corr} - E^{eq,a3}\right)\right] \quad \text{…… (3.27)}$$

$$i_{c1} = i_{o,c1} f_1 \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{corr} - E^{eq,c1}\right)\right] \quad \text{….. (3.28)}$$

$$i_{c2} = i_{o,c2} f_2 \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{corr} - E^{eq,c2}\right)\right] \quad \text{…… (3.29)}$$

$$i_{c3} = i_{o,c3} f_3 \exp\left[\frac{-F\alpha_c n}{RT}\left(E^{corr} - E^{eq,c3}\right)\right] \quad \text{….. (3.30)}$$

3.5 Numerical Methods

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

3.5.1 Comparing With Experimental Results [48]:

a- Estimating equilibrium potentials for metals and for hydrogen from equation (3.1) at T of 30, 45 and 60^{o}C. For different pH values equation (3.3) is used to calculate hydrogen ion concentrations.

b- The exchange current density is calculated from equation (3.9) for three values of temperatures (30, 45 and 60^{o}C).

c- The variation of exchange current density with medium’s concentration is calculated from equation (3.12) at T of 30, 45 and 60^{0}C.

d- For departure from equilibrium state (activated state), the current density for each cathodic and anodic reaction is calculated from equations (3.5 and 3.6) for free (single) metal corrosion at pH= 0.7.

e- The galvanic current density for binary system for each cathodic and anodic reaction is estimated from equations (3.18 to 3.21) at T of 30, 45 and 60°C.

f- In all the above processes the corrosion's potential is unknown as the current densities, so at first assuming a value to corrosion potential then substituting it in corrosion currents' equations (3.18 to 3.21),then in equation (3.14), the program examine the difference between the summation of anodic and cathodic current density, then a new value of corrosion potential is assumed until the difference becomes smaller, this step is repeated to have a minimum difference.

g- The program is repeated for different area fractions for binary system for each metal.

3.5.2 Programs' Results:

a- First the program is set to estimate corrosion current densities and corrosion potential for free corrosion for pH values of (1, 2 and 3), and for temperatures of(20, 30, 40, 50 and 60 °C).

b- Then the program is set to calculate corrosion current density (at basis 1 cm^2) and corrosion potential for ternary system for pH values of 1, 2 and 3, and for temperatures of 20, 30, 40, 50 and 60 °C for different area fractions as shown in the following table:

Table 3.1 Ternary Systems and the Variation of Area Fractions of Metals Used

Systems	Area fraction of zinc	Area fraction of iron	Area fraction of copper
Systems 1	0.1	0.8	0.1
Systems 2	0.5	0.4	0.1
Systems 3	0.1	0.4	0.5
Systems 4	0.8	0.1	0.1
Systems 5	0.1	0.1	0.8
Systems 6	0.1	0.5	0.4
Systems 7	0.4	0.1	0.5

c- The same procedure that have been done in binary system to calculate the corrosion current and corrosion potential were repeated using the equations (3.25 to 3.30), and equation (3.23).

CHAPTER FOUR

RESULTS

4.1 Free Corrosion of metals:

4.1.1 Free Corrosion of copper:

4.1.1.1 Free Corrosion of copper at pH=0.7:

In the following table the corrosion potential is compared with experimental work [48]:

Table 4.1 comparison of corrosion potential calculated with experimental of copper at pH=0.7

E_{corr}(mV)	E_{exp}(mV)	$I_{H2/cu}$(μA)	I_{cu} (μA)	T(°C)	AAPE
-70.83	-73	-799.57	799.56	30	2.97
-81.45	-78	-1745.83	1745.8	45	4.42
-91.51	-85	-3518.95	3518.9	60	7.96

4.1.1.2 Free Corrosion of copper at pH=1-3 and T=20-60°C:

Table 4.2 effect of temperature on copper at pH=1

E_{corr}(mV)	$I_{H2/cu(}$μA)	I_{cu}(μA)	T(°C)
-135.05	-547.49	547.49	20
-141.34	-855.3	855.3	30
-147.29	-1305.7	1305.7	40
-152.96	-2011.6	2011.6	50
-158.41	-3033	3033	60

Table 4.3 effect of temperature on copper at pH=2

E_{corr}(mV)	$I_{H2/cu}$(μA)	I_{cu}(μA)	T(°C)
-120.22	-307.62	307.62	20
-127.75	-468.15	468.15	30
-135.22	-803.63	803.63	40
-142.63	-1365.7	1365.7	50
-149.96	-2296.4	2296.4	60

Table 4.4 effect of temperature on copper at pH=3

E_{corr}(mV)	$I_{H2/cu(}$µA)	I_{cu}(µA)	T(°C)
-100.99	-160.1	160.1	20
-107.94	-294.3	294.3	30
-114.90	-546.25	546.25	40
-121.85	-1031.5	1031.5	50
-128.80	-1829.0	1829.0	60

4.1.2 Free Corrosion of Iron:

4.1.2.1 Free Corrosion of Iron at pH=0.7:

In the following table the corrosion potential is compared with experimental work [48]:

Table 4.5 comparison of corrosion potential calculated with experimental of iron at pH=0.7

E_{corr}(mV)	E_{exp}(mV)	$I_{H2/fe}$(μA)	I_{fe} (μA)	T(°C)	AAPE
-387.99	-510	-18421.88	18421.88	30	23.92
-396.99	-498	-26816.22	26816.22	45	20.28
-404.99	-524	-37085.4	37085.4	60	22.71

4.1.2.2 Free Corrosion of iron at pH=1-3 and T=20-60°C:

Table 4.6 effect of temperature on iron at pH=1

E_{corr}(mV)	$I_{H2/fe}$(μA)	I_{fe}(μA)	T(°C)
-386.99	-5480.35	5480.35	20
-392.99	-7167.60	7167.60	30
-398.99	-9214.90	9214.90	40
-404.99	-11664.1	11664.1	50
-410.99	-14556.7	14556.7	60

Table 4.7 effect of temperature on iron at pH=2

E_{corr}(mV)	$I_{H2/fe}$(μA)	I_{fe}(μA)	T(°C)
-371.99	-128.76	128.76	20
-382.99	-187.15	187.15	30
-392.99	-260.72	260.72	40
-402.99	-355.83	355.83	50
-411.99	-468.41	468.41	60

Table 4.8 effect of temperature on iron at pH=3

E_{corr}(mV)	$I_{H2/fe}$(μA)	I_{fe}(μA)	T(°C)
-316.99	-1.37	1.37	20
-326.99	-2.02	2.02	30
-336.99	-2.91	2.91	40
-346.99	-4.11	4.11	50
-356.99	-5.68	5.68	60

4.1.3 Free Corrosion of Zinc:

4.1.3.1 Free Corrosion of Zinc at pH=0.7:

In the following table the corrosion potential is compared with experimental work [48]:

Table 4.9 corrosion potential and current of zinc at pH=0.7

E_{corr}(mV)	E_{exp}(mV)	$I_{H2/zn}$(μA)	I_{zn} (μA)	T(°C)	AAPE
-814.16	-756	-62618.64	62618.64	30	7.69
-829.28	-786	-75437.17	75437.17	45	5.51
-844.40	-815	-92571.05	92571.05	60	3.61

4.1.3.2 Free Corrosion of Zinc at pH=1-3 and T=20-60°C:

Table 4.10 effect of temperature on zinc at pH=1

E_{corr}(mV)	$I_{H2/zn(}$μA)	I_{zn}(μA)	T(°C)
-809.91	-24850.05	24850.05	20
-820.19	-28081.05	28081.05	30
-830.47	-31981.04	31981.04	40
-840.75	-36736.66	36736.66	50
-851.03	-42600.59	42600.59	60

Table 4.11 effect of temperature on zinc at pH=2

E_{corr}(mV)	$I_{H2/zn(}$μA)	I_{zn}(μA)	T(°C)
-809.91	-1153.11	1153.11	20
-820.19	-1303.09	1303.09	30
-830.47	-1484.11	1484.11	40
-840.75	-1704.84	1704.84	50
-851.03	-1978.02	1978.02	60

Table 4.12 effect of temperature on zinc at pH=3

E_{corr}(mV)	$I_{H2/zn(}$μA)	I_{zn}(μA)	T(°C)
-848.48	-53.20	53.20	20
-860.05	-60.16	60.16	30
-871.61	-68.57	68.57	40
-883.17	-78.85	78.85	50
-894.72	-91.44	91.44	60

4.2 Galvanic Corrosion of Metals:

4.2.1 Galvanic Corrosion of Copper and Iron:

4.2.1.1 Galvanic Corrosion of Copper and Iron at Area Ratio=0.5:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.13 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and iron at area ratio=0.5 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)	AAPE
-684.74	-672.18	20.45	2822.49	-2361.35	-481.59	30	1.86
-707.76	-701.48	61.51	2961.04	-2430.57	-591.53	45	0.89
-728.68	-723.92	124.01	3204.32	-2494.57	-839.99	60	0.65

4.2.1.2 Galvanic Corrosion of Copper and Iron at Area Ratio=1:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.14 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and iron at area ratio=1 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)	AAPE
-667.19	-659.98	12.31	2633.04	-2208.94	-436.41	30	1.09
-690.17	-688.36	43.16	2841.42	-2361.3	-523.27	45	0.26
-711.09	-701.48	82.51	3286.29	-2547.41	-821.38	60	0.13

4.2.1.3 Galvanic Corrosion of Copper and Iron at Area Ratio=2:

In the following table the corrosion potential compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.15 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and iron at area ratio=2 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)	AAPE
-649.64	-657.53	7.823	2410.50	-2163.11	-239.56	30	1.19
-672.62	-682.66	13.92	2600.84	-2274.49	-340.27	45	1.47
-693.54	-742.99	37.41	2994.31	-2497.21	-534.51	60	6.65

4.2.2 Galvanic Corrosion of Copper and Zinc:

4.2.2.1 Galvanic Corrosion of Copper and Zinc at Area Ratio=0.5:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.16 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and zinc at area ratio=0.5 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{zn}(μA)	$I_{H2/cu}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-1008.21	-1109.19	2.116	20087.92	-20088.14	-1.895	30	9.10
-1162.43	-1187.32	6.259	21466.38	-21468.51	-4.130	45	2.09
-1192.72	-1216.62	13.843	22516.43	-22519.33	-10.942	60	1.96

4.2.2.2 Galvanic Corrosion of Copper and Zinc at Area Ratio=1:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.17 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and zinc at area ratio=1 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{zn}(μA)	$I_{H2/cu}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-999.51	-1057.92	0.846	15276.62	-15276.68	-0.651	30	5.52
-1199.71	-1245.91	1.273	15537.89	-15538.24	-0.924	45	3.71
-1273.28	-1155.58	4.950	15809.79	-15813.20	-1.540	60	10.18

4.2.2.3 Galvanic Corrosion of Copper and Zinc at Area Ratio=2:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.18 comparison of corrosion potential calculated with experimental of galvanic coupling of copper and zinc at area ratio=2 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{cu}(μA)	I_{zn}(μA)	$I_{H2/cu}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-976.53	-998.53	0.009	10472.43	-10472.44	-0.010	30	2.20
-1089.47	-1136.05	0.025	10860.99	-10860.95	-0.017	45	4.10
-1167.83	-1281.61	0.209	11493.62	-11493.73	-0.101	60	8.87

4.2.3 Galvanic Corrosion of Iron and Zinc:

4.2.3.1 Galvanic Corrosion of Iron and Zinc at Area Ratio=0.5:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.19 comparison of corrosion potential calculated with experimental of galvanic coupling of zinc and iron at area ratio=0.5 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{fe}(μA)	I_{zn}(μA)	$I_{H2/fe}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-1080.42	-1067.7	87.92	10882.35	-10943.86	-26.41	30	1.19
-1171.29	-1165.35	99.65	12684.64	-12743.24	-41.05	45	5.09
-1204.61	-1089.66	110.04	17853.26	-17892.18	-71.12	60	10.55

4.2.3.2 Galvanic Corrosion of Iron and Zinc at Area Ratio=1:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.20 comparison of corrosion potential calculated with experimental of galvanic coupling of zinc and iron at area ratio=1 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{fe}(μA)	I_{zn}(μA)	$I_{H2/fe}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-1023.80	-1015.21	51.34	9856.65	-9905.94	-1.950	30	0.84
-1081.97	-896.79	72.64	11094.17	-11152.70	-14.116	45	20.64
-1157.62	-1136.05	101.02	1285.43	-1349.72	-36.73	60	1.89

4.2.3.3 Galvanic Corrosion of Iron and Zinc at Area Ratio=2:

In the following table the corrosion potential is compared with experimental work [48] at pH=0.7 in deaerated hydrochloric acid:

Table 4.21 comparison of corrosion potential calculated with experimental of galvanic coupling of zinc and iron at area ratio=2 and pH=0.7

$E_{corr.}$(mV)	E_{exp}(mV)	I_{fe}(μA)	I_{zn}(μA)	$I_{H2/fe}$(μA)	$I_{H2/zn}$(μA)	T(°C)	AAPE
-998.26	-995.01	21.33	8954.38	-8975.09	-0.621	30	3.26
-1206.48	-1192.21	39.51	10069.47	-10105.26	-3.724	45	1.19
-1227.55	-953.0	71.35	12299.68	-12360.11	-10.92	60	28.80

4.3 Ternary Corrosion of Iron and Zinc and Copper:

4.3.1 System 1:

Area fraction of zinc=0.1, of copper=0.1 and that of iron=0.8: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.22 results for galvanic ternary system 1 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-843.87	626.62	1.08E-10	2.11E-03	-7.62E-03	-541.45	-85.17	20
-849.14	878.42	2.02E-10	0.00301	-0.00921	-750.22	-128.21	30
-854.41	1268.4	3.01E-10	0.00402	-0.01213	-1044.2	-224.21	40
-859.68	1808.4	4.02E-10	0.0051	-0.01423	-1417.68	-390.72	50
-864.95	2600.82	6.01E-10	0.00714	-0.01542	-1931.7	-668.28	60

Table 4.23 results for galvanic ternary system 1 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-818.25	403.64	7.68E-10	0.11E-03	-5.62E-03	-338.47	-65.17	20
-823.52	677.83	9.97E-10	0.00981	-0.00731	-569.61	-108.21	30
-828.79	1014.51	1.25E-10	0.00212	-0.01084	810.30	-204.21	40
-834.06	1572.36	2.19E-10	0.0031	-0.01219	-1201.64	-370.72	50
-839.33	2379.97	4.26E-10	0.00526	-0.0134	-1731.69	-648.28	60

Table 4.24 results for galvanic ternary system 1 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-792.63	225.51	6.61E-10	0.00048	-4.62E-03	-190.36	-35.15	20
-797.9	475.16	6.84E-10	0.000781	-0.00631	-408.25	-66.91	30
-803.17	814.06	8.25E-10	0.0009	-0.0983	-655.91	-158.05	40
-808.44	1246.61	1.17E-9	0.0011	-0.01107	-915.56	-331.04	50
-813.71	2179.72	3.26E-9	0.00326	-0.0120	-1582.55	-597.16	60

4.3.2 System 2:

Area fraction of zinc=0.5, of copper=0.1 and that of iron=0.4: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.25 results for galvanic ternary system 2 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-893.27	2651.79	8.34E-12	8.70E-06	-5.31E-03	-1717.86	-933.93	20
-899.59	3147.64	1.41E-11	1.06E-05	-7.30E-03	-1.95E+03	-11.97E+02	30
-905.81	3834.73	2.44E-11	1.35E-05	-9.61E-03	-2.347E+03	-1.487E+03	40
-912.03	4719.92	4.04E-11	1.75E-05	-1.25E-02	-2.86E+03	-1.86E+03	50
-917.25	5981.38	6.72E-11	2.27E-05	-1.61E-02	-3.664E+03	-2.317E+03	60

Table 4.26 results for galvanic ternary system 2 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-849.5	1995.73	4.55E-12	6.71E-06	-3.31E-03	-1.42E+03	-5.757E+02	20
-854.77	2354.51	8.62E-12	8.36E-06	-5.30E-03	-1.57E+03	-7.836E+02	30
-860.04	2861.02	1.62E-11	1.10E-05	-7.61E-03	-1.84E+03	-1.021E+03	40
-865.31	3796.19	3.11E-11	1.45E-05	-1.05E-02	-2.36E+03	-1436.19	50
-870.58	4816.26	5.85E-11	1.87E-05	-1.41E-02	-3.06E+03	-1.756E+03	60

Table 4.27 results for galvanic ternary system 2 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.6	1284.35	1.26E-12	4.68E-06	-1.31E-03	-1.02E+03	-3.644E+02	20
-852.8	1789.72	4.61E-12	6.55E-06	-3.27E-03	-1.33E+03	-4.597E+02	30
-859	2231.27	1.27E-11	9.05E-06	-0.00561	-1598.28	-632.99	40
-865.3	2911.98	2.52E-11	1.25E-05	-8.55E-03	-1.76E+03	-1.152E+03	50
-871.5	4153.01	4.75E-11	1.67E-05	-1.21E-02	-2.54E+03	-1.613E+03	60

4.3.3 System 3:

Area fraction of zinc=0.1, of copper=0.5 and that of iron=0.4: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.28 results for galvanic ternary system 3 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-849.5	1205.81	6.6E-19	7.21E-14	-5.31E-03	-723.885	-481.92	20
-854.77	1573.41	7.8E-19	9.1E-14	-7.30E-03	-9.51E+02	-6.22E+02	30
-860.04	2125.61	9.3E-19	1.3E-13	-9.61E-03	-1.265E+03	-8.61E+02	40
-865.31	2814.35	1.1E-18	3.2E-13	-1.25E-02	-1.634E+03	-1.18E+03	50
-870.58	3712.92	1.5E-18	5.4E-13	-1.61E-02	-2.063E+03	-1.65E+03	60

Table 4.29 results for galvanic ternary system 3 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	995.73	4.6E-19	5.1E-14	-3.31E-03	-613.73	-381.97	20
-852.81	1354.61	5.5E-19	7.5E-14	-5.30E-03	-882.60	-4.72E+02	30
-859.03	1829.52	6.8E-19	8.1E-14	-7.61E-03	-1168.51	-6.61E+02	40
-865.25	2471.19	8.1E-19	9.4E-14	-1.05E-02	-1472.94	-998.24	50
-871.47	3338.26	1.2E-18	1.8E-13	-1.41E-02	-1888.24	-1.45E+03	60

Table 4.30 results for galvanic ternary system 3 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	684.35	2.6E-19	3.1E-14	-1.31E-03	-448.74	-235.61	20
-852.81	979.82	4.2E-19	5.2E-14	-3.27E-03	-607.82	-3.72E+02	30
-859.03	1356.51	6.6E-19	7.4E-14	-0.00561	-845.29	-520.22	40
-865.25	1911.61	7.5E-19	9.1E-14	-8.55E-03	-1113.91	-7.98E+02	50
-871.47	2653	9.1E-19	1.4E-13	-1.21E-02	-1.43E+03	-1.25E+03	60

4.3.4 System 4:

Area fraction of zinc=.08, of copper=0.1 and that of iron=0.1: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.31 results for galvanic ternary system 4 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-942.16	3075.79	8.34E-12	8.70E-06	-5.31E-03	-2816.6	-259.19	20
-947.43	3599.58	1.41E-11	1.06E-05	-7.30E-03	-3142.34	-457.24	30
-952.7	4312.81	2.44E-11	1.35E-05	-9.61E-03	-3608.04	-704.77	40
-957.97	5172.71	4.04E-11	1.75E-05	-1.25E-02	-4206.17	-966.52	50
-963.24	6254.38	6.72E-11	2.27E-05	-1.61E-02	-5024.35	-1230.01	60

Table 4.32 results for galvanic ternary system 4 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	2775.79	4.55E-12	6.71E-06	-3.31E-03	-2526.94	-248.85	20
-852.81	3299.58	8.62E-12	8.36E-06	-5.30E-03	-3022.93	-276.64	30
-859.03	4012.81	1.62E-11	1.10E-05	-7.61E-03	-3517.90	-494.9	40
-865.25	4872.71	3.11E-11	1.45E-05	-1.05E-02	-4018.48	-854.221	50
-871.47	5954.38	5.85E-11	1.87E-05	-1.41E-02	-4824.25	-1130.12	60

Table 4.33 results for galvanic ternary system 4 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	2475.79	1.26E-12	4.68E-06	-1.31E-03	-2319.94	-155.85	20
-852.81	2999.58	4.61E-12	6.55E-06	-3.27E-03	-2826.94	-172.64	30
-859.03	3712.81	1.27E-11	9.05E-06	-0.00561	-3307.71	-405.09	40
-865.25	4572.71	2.52E-11	1.25E-05	-8.55E-03	-3818.51	-754.19	50
-871.47	5454.38	4.75E-11	1.67E-05	-1.21E-02	-4657.38	-796.99	60

4.3.5 System 5:

Area fraction of zinc=0.1, of copper=0.8 and that of iron=0.1: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.34 results for galvanic ternary system 5 at pH=1

E_{corr}(mV)	I_{zn}(µA)	I_{cu}(µA)	I_{fe}(µA)	$I_{H2/zn}$(µA)	$I_{H2/cu}$(µA)	$I_{H2/fe}$(µA)	T(°C)
-822.24	489.38	6.6E-19	7.21E-14	-5.31E-03	-300.84	-188.54	20
-827.51	704.67	7.8E-19	9.1E-14	-7.30E-03	-506.17	-198.5	30
-832.78	1028.92	9.3E-19	1.3E-13	-9.61E-03	-743.27	-285.65	40
-838.05	1585.64	1.1E-18	3.2E-13	-1.25E-02	-1114.37	-471.27	50
-843.32	2353.55	1.5E-18	5.4E-13	-1.61E-02	-1848.76	-504.79	60

Table 4.35 results for galvanic ternary system 5 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-856.88	389.38	4.6E-19	5.1E-14	-3.31E-03	-210.51	-178.87	20
-862.15	604.67	5.5E-19	7.5E-14	-5.30E-03	-405.16	-199.51	30
-867.42	928.92	6.8E-19	8.1E-14	-7.61E-03	-643.54	-285.38	40
-872.69	1485.64	8.1E-19	9.4E-14	-1.05E-02	-1014.5	-471.13	50
-877.96	2253.55	1.2E-18	1.8E-13	-1.41E-02	-1759.8	-493.74	60

Table 4.36 results for galvanic ternary system 5 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	289.38	2.6E-19	3.1E-14	-1.31E-03	-190.31	-99.07	20
-852.81	504.67	4.2E-19	5.2E-14	-3.27E-03	-385.62	-119.05	30
-859.03	828.92	6.6E-19	7.4E-14	-0.00561	-630.28	-198.64	40
-865.25	1385.76	7.5E-19	9.1E-14	-8.55E-03	-987.61	-398.15	50
-871.47	2042.19	9.1E-19	1.4E-13	-1.21E-02	-1618.10	-424.09	60

4.3.6 System 6:

Area fraction of zinc=0.1, of copper=0.4 and that of iron=0.5: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.37 results for galvanic ternary system 6 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-856.88	1462.88	9.6E-11	5.2E-10	-7.62E-03	-859.89	-602.98	20
-862.15	1851.92	9.9E-11	5.4E-10	-0.00921	-956.71	-895.21	30
-867.42	2446.35	1.2E-10	5.5E-10	-0.01213	-1374.88	-1071.47	40
-872.69	3168.28	1.5E-11	5.8E-10	-0.01423	-1957.65	-1210.57	50
-877.96	4084.19	1.7E-11	6.3E-10	-0.01542	-2487.18	-1596.99	60

Table 4.38 results for galvanic ternary system 6 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	1262.88	8.4E-11	4.2E-10	-5.62E-03	-739.17	-537.70	20
-852.81	1651.92	8.6E-11	4.4E-10	-0.00731	-993.72	-658.19	30
859.03	2246.35	8.9E-11	4.5E-10	-0.01084	-1320.87	-925.47	40
865.25	2968.82	9.1E-11	4.8E-10	-0.01219	-1827.32	-1141.49	50
871.47	3824.29	9.4E-11	5.3E-10	-0.0134	-2425.32	-1398.96	60

Table 4.39 results for galvanic ternary system 6 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	862.88	7.5E-11	3.2E-10	-4.62E-03	-641.31	-221.56	20
852.81	1451.92	7.7E-11	3.4E-10	-0.00631	-894.61	-557.30	30
859.03	2046.35	8.0E-11	3.5E-10	-0.00983	-1296.53	-749.81	40
865.25	2768.14	8.2E-11	3.8E-10	-0.01107	-1786.38	-981.75	50
871.47	3484.27	8.6E-11	4.3E-10	-0.0120	-2378.45	-1105.81	60

4.3.5 System 7:

Area fraction of zinc=0.4, of copper=0.5 and that of iron=0.1: pH=1 to 3 and for temperatures=20 to 60° in deareated hydrochloric acid:

Table 4.40 results for galvanic ternary system 7 at pH=1

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-878.93	2205.81	1.06E-10	7.21E-14	6.8E-4	-1204.60	-1001.21	20
-884.2	2673.41	1.25E-10	9.1E-14	7.1E-4	-1424.53	-1248.88	30
-889.47	3335.61	1.34E-10	1.3E-13	7.3E-4	-1942.47	-1393.14	40
-894.74	4054.35	1.46E-10	3.2E-13	7.7E-4	-3028.58	-1025.77	50
-900.01	4982.92	1.75E-10	5.4E-13	8.1E-4	-3648.91	-1334.01	60

Table 4.41 results for galvanic ternary system 7 at pH=2

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	2005.81	9.1E-11	5.1E-14	-5.4E-4	-1104.6	-901.21	20
852.81	2473.41	1.1E-10	7.5E-14	-5.7E-4	-1334.51	-1138.9	30
859.03	3135.61	1.2E-10	8.1E-14	-6.1E-4	-1851.46	-1284.15	40
865.25	3854.35	1.3E-10	9.4E-14	-6.5E-4	-2517.48	-1336.87	50
871.47	4782.92	1.5E-10	1.8E-13	-6.9E-4	-3345.11	-1437.81	60

Table 4.42 results for galvanic ternary system 7 at pH=3

E_{corr}(mV)	I_{zn}(μA)	I_{cu}(μA)	I_{fe}(μA)	$I_{H2/zn}$(μA)	$I_{H2/cu}$(μA)	$I_{H2/fe}$(μA)	T(°C)
-846.59	1805.81	8.6E-11	3.1E-14	-4.1E-4	-1028.79	-777.02	20
852.81	2473.41	8.8E-11	5.2E-14	-4.4E-4	-1947.08	-526.33	30
859.03	3135.61	9.1E-11	7.4E-14	-4.9E-4	-2439.57	-696.04	40
865.25	3654.35	9.3E-11	9.1E-14	-5.3E-4	2846.67	-807.68	50
871.47	4582.92	9.6E-11	1.4E-13	-5.7E-4	-3271.24	-1311.68	60

CHAPTER FIVE

DISCUSSION

The results that obtained in chapter four will be discussed in this chapter. Generally any deviation between experimental work of Al-Hadithy [62] and the calculated results may be due to the initial corrosion data such as exchange current density of each metal, exchange current density of hydrogen evolution on each metal and activation energies of metals used in the present work as taken from various references.

5.1 Free Corrosion of metals:

5.1.1 Comparison with Experimental Results [48]:

The corrosion potential of copper is compared with experimental work of Al-Hadithy [48] in deaerated pH =0.7 hydrochloric acid at temperatures of 30, 45 and 60°C as tabulated in table 4.1 and plotted in fig. 5.1. It is clear that the corrosion potential decreased as temperature increased at constant pH value, i.e. fixed H^+ concentration. The effect of temperature is first on equilibrium potential (equations 3.1 and 3.2), then on exchange current density (equation 3.9) finally on corrosion current and potential (equation 3.4). Therefore: as temperature increases the corrosion potential decreases, i.e. shifted to the more active state (more negative). This can be ascribed to the decreased equilibrium potential and to the increased exchange current density which in turn increased the anodic and cathodic currents (both currents are equal in order to reach equilibrium state as it is obvious from equation 3.7); by this way the corrosion potential decreased because it is inversely proportional to the current.

Figure 5.1 reveals good agreement between calculated results and experimental work of Al-Hadithy [48]. At 30°C the calculated corrosion potential is little higher than the experimental one, while at high temperature (60°C) the calculated corrosion potential became lower than the experimental one.

The same temperature effect on metal's corrosion potential is found on other used two metals (iron and zinc) as tabulated in tables (4.6 and 4.11).

Appendix E shows in details a sample of calculations of T=30°C and pH=0.7, the corrosion potential that have been found is the same recorded by the program, but there is little deviation of anodic and cathodic currents equals to 0.3% error.

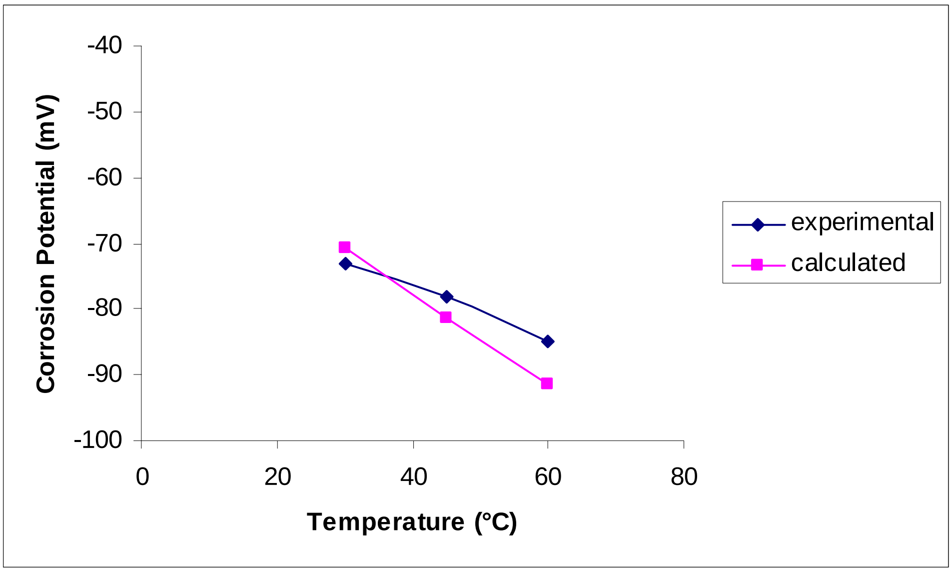

Figure 5.1 Comparison of theoretical results with experimental work for corrosion of copper at pH=0.7

The anodic and cathodic currents (shown in fig. 5.2) increases exponentially as temperature increased (equations 3.5 and 3.6). The calculated results for copper (table 4.1 and plotted in fig. 5.2) showed this effect in deaerted pH =0.7 hydrochloric acid at temperatures 30, 45 and 60°C. The currents are at equal currents (equation 3.7) so the curves are identical. Anodic current is the copper oxidation and the cathodic current is the hydrogen evolution current on copper surface. The same trend is noticed for iron and zinc (table 4.7 and 4.12).

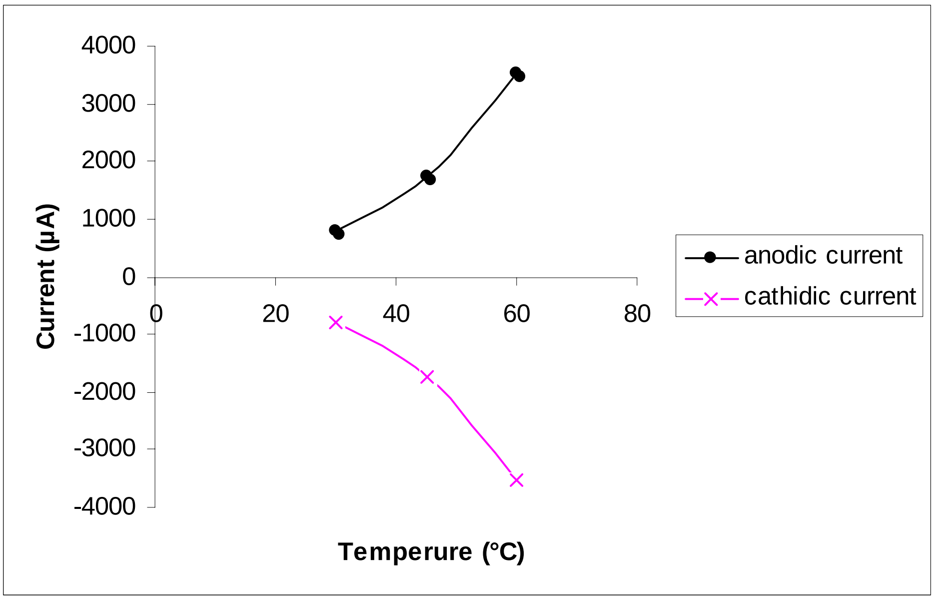

Figure 5.2 The anodic and cathodic current variation with temperature at pH=0.7 for copper

5.1.2 Free Corrosion at pH=1-3 and T=20-60°C

The corrosion current and potential obtained from theoretical calculation at pH=1, 2 and 3 and temperatures of 20,30,40,50 and 60°C are shown in $\mathrm{fig}_{\mathrm{s}}$. 5.3 and 5.4:

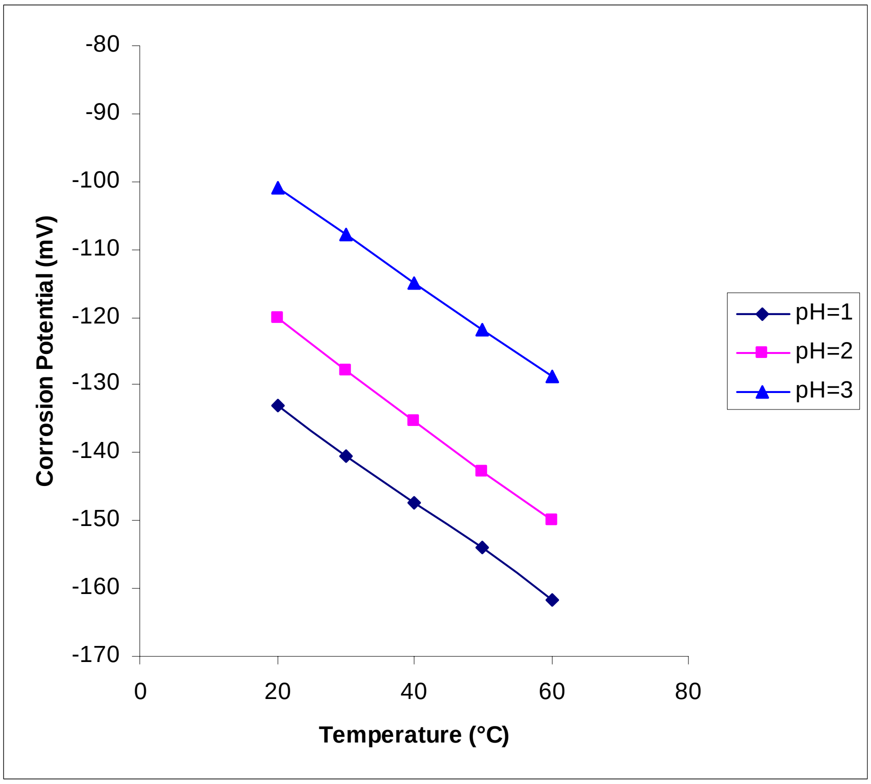

Figure 5.3 Corrosion potential of copper versus temperature at pH=1, 2 and 3

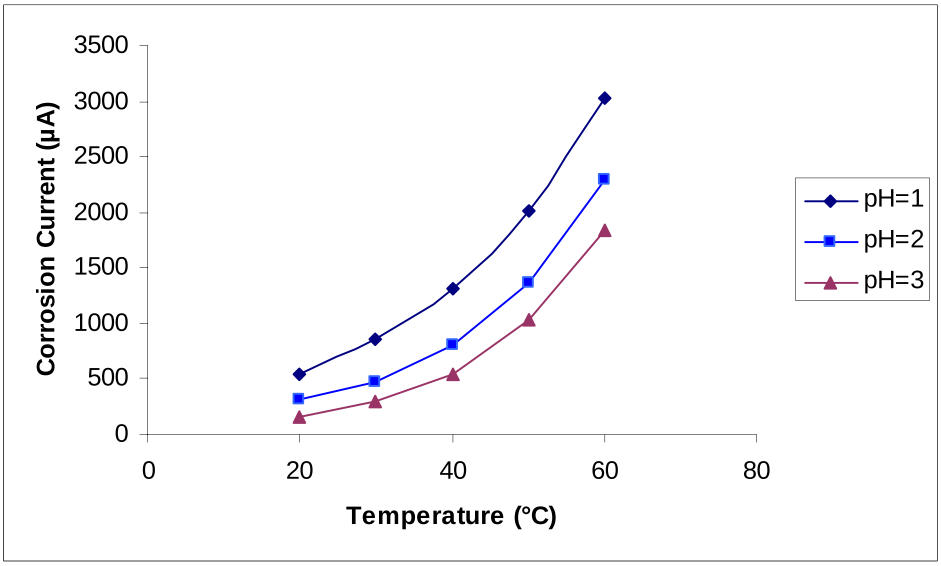

Figure 5.4 The corrosion current of copper versus temperature at pH=1, 2 and 3

It is obvious from these figures that the corrosion potential decreases with increasing temperature, while the corrosion current increases with temperature at constant pH value. Increasing the pH increases the potential but decreases the current. This is due to decreased H^+ concentration shifting the corrosion potential to more positive (less active state). Decreasing H^+ concentration leads to decrease corrosion current and corrosion rate.

5.2 Galvanic Corrosion of Metals

5.2.1 Coupling of Metals

The calculated galvanic corrosion potential compared with the experimental work [48] in deaerted hydrochloric acid of pH=0.7 at temperatures 30, 45 and 60°C is shown in fig. 5.4. Figure 5.4 shows an example of coupling of metals when copper coupled to iron at pH=0.7 at area ratio of cathode to anode =0.5. The calculated results are in good agreement with experimental work. As in free corrosion the galvanic corrosion potential decreases whenever increasing temperature. The effect of temperature is first on equilibrium potential, then on exchange current density, finally on corrosion current and potential.

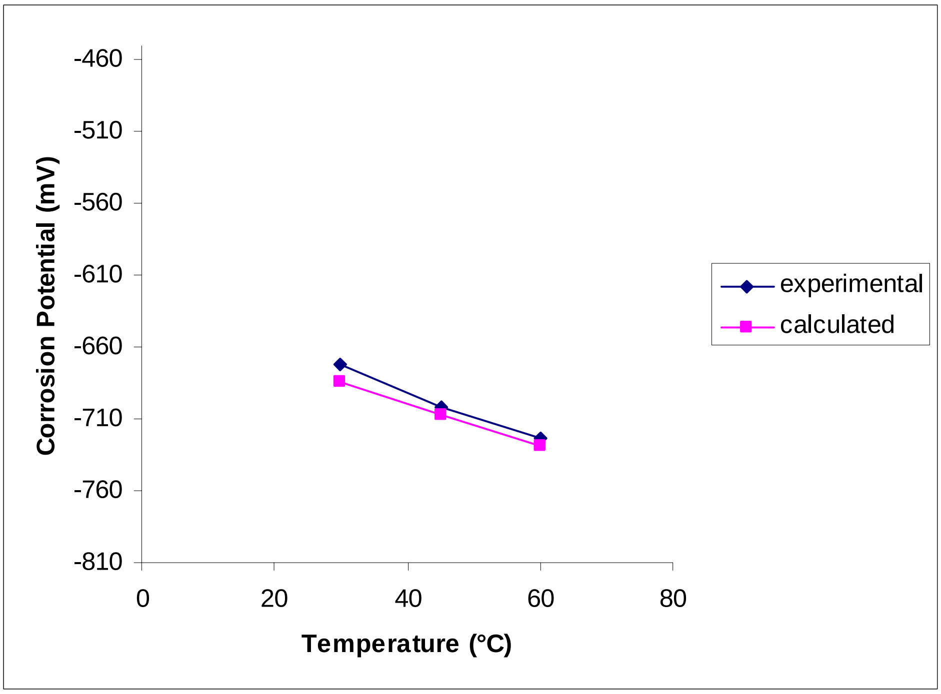

Figure 5.5 Comparison of calculated results of galvanic corrosion potential with the experimental work of copper and iron at pH=0.7 and area ratio= 0.5

The effect of area ratio of cathode to anode plays an important rule in galvanic coupling. So increasing the ratio of cathode (copper) to the anode (iron) increases the corrosion rate of iron because of the corrosion potential increase (shifted to more positive side) by this way the anodic metal became more active. Increasing the cathodic exposed area increases the electron transfer rate, leading to increase the cathodic reaction (hydrogen evolution) and this will anodic dissolution of iron. Figures 5.6 and 5.7 show the effect of area ratio (cathode/anode) on corrosion potential and on corrosion current respectively. The same trend is noticed on the other two couples (copper and zinc couple and iron and zinc couple) as shown in tables 4.16 to 4.21.

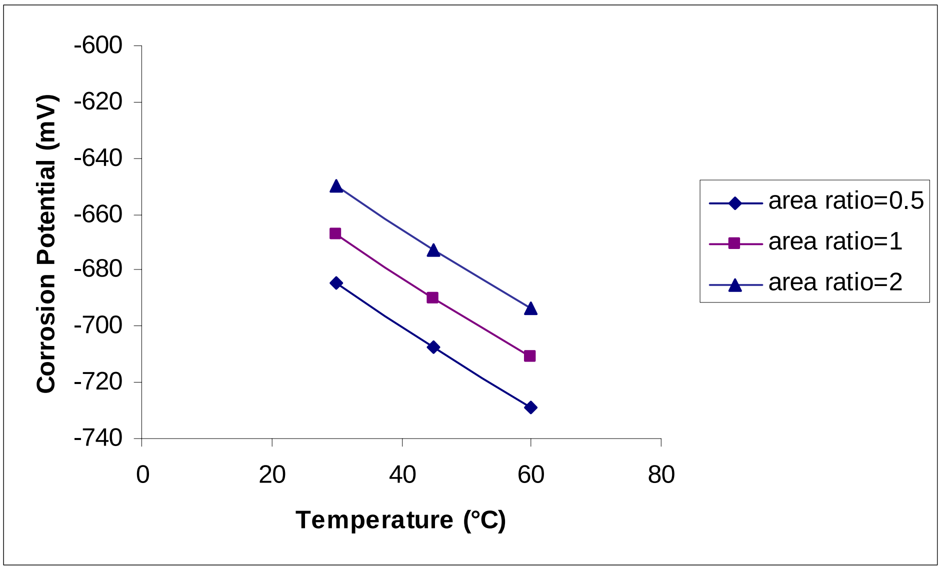

Figure 5.6 The effect of area ratio on galvanic corrosion potential of copper and iron couple at different temperatures and pH=0.7

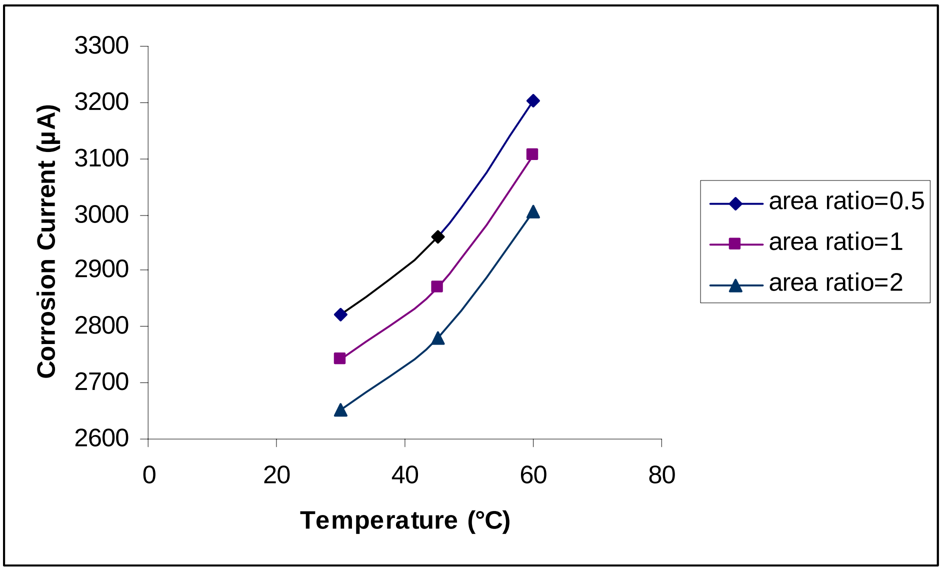

Figure 5.7 The effect of area ratio on anodic corrosion current of iron for copper and iron couple at different temperatures

On each metal in galvanic cell separate cathodic and anodic reactions occur, the anodic reaction represents the metal dissolution (oxidation reaction which involve electron loss and ion exchange to the medium) and the cathodic reaction represents the hydrogen evolution (reduction of hydrogen ions from the solution by gaining the electrons to produce hydrogen gas). The anodic reaction on the cathodic metal (less active metal as a copper here) is little, whears it is higher at the anodic metal (more active metal as iron here), this is because the equilibrium potential of anodic metal is less than that of cathodic metal. In a reverse order, the cathodic reaction on the cathodic metal is much higher than that on the anodic metal which in the case of zinc becomes negligible because of its relatively small exchange current density (1.6 E-7 A/cm^2). Figure 5.8 shows the effect of temperature on the oxidation and reduction currents.

Figure 5.8 shows the effect of temperature on the oxidation (anodic) and reduction (cathodic) currents as follows: increasing temperature will highly increase anodic current of more active metal (as iron in fig. 5.8), slightly increase anodic current of less active metal (as copper in fig. 5.8), increases the cathodic reaction of copper (hydrogen evolution on copper) and finally slightly increases the cathodic current of iron (hydrogen evolution on iron). Figure 5.8 reveals that the hydrogen evolution current on iron and copper dissolution are very little. This trend holds for all area ratios in galvanic systems considered.

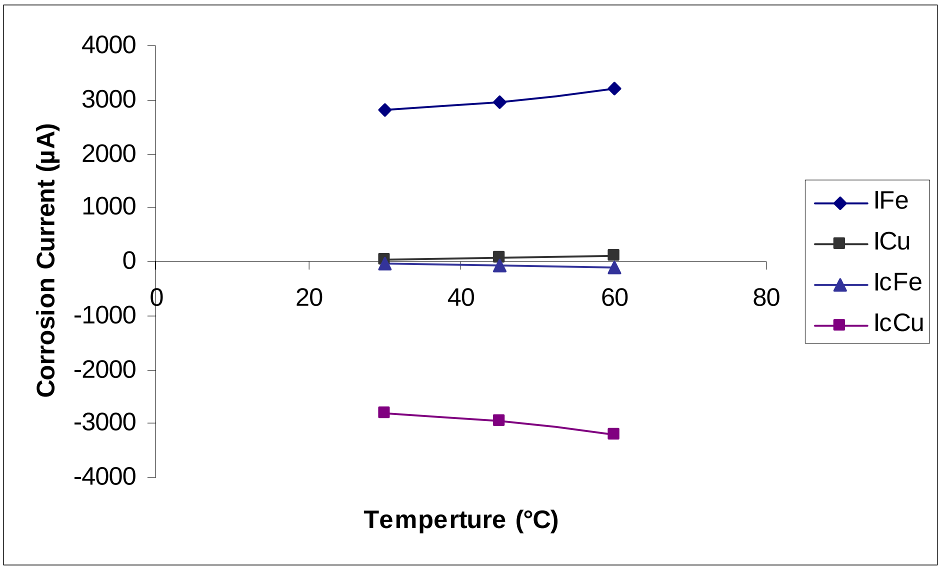

Figure 5.8 Anodic and cathodic corrosion currents of iron and copper at area ratio=0.5 at pH=0.7

5.2.2 Ternary Systems:

The metals used in this work are assumed to be joined in deaerted hydrochloric acid in different temperatures, pH values and area fractions (area of one metal to total areas of metals used). The metals considered are copper, iron and zinc. The results are discussed in this chapter.

Generally, the corrosion potential decrease with increasing temperature i.e. shifted to more negative values at fixed pH value. Increasing pH value increases the corrosion potential for ternary system as shown in fig. 5.9 for system 1 (area fractions are as follows: zinc =0.1, copper=0.1, iron= 0.8)

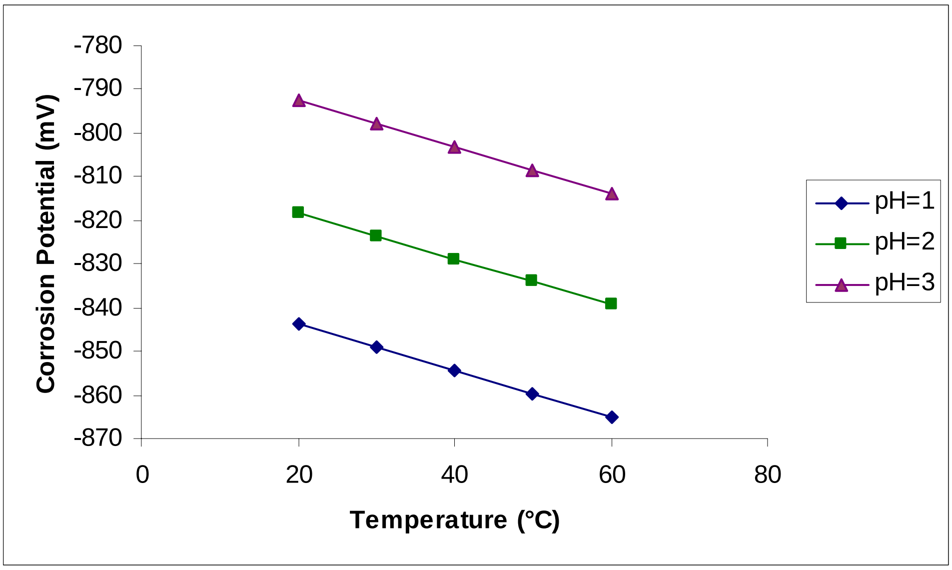

Figure 5.9 Corrosion potential of system 1 for different pH values and temperatures

Figure 5.9 reveals that for ternary system, increasing the temperature leads to decrease the corrosion potential by decreasing equilibrium potentials and increasing hydrogen exchange current densities.

Also the higher the pH is the higher galvanic corrosion potential; i.e. the corrosion potential becomes more positive. This can be reasoned to the decrease in hydrogen ion concentration with increasing pH (equation 3.3)

Figure 5.10 shows that the corrosion current exponentially increased with increasing temperature and this increase is highest at pH=1 but becomes less at lower pH values, because increasing pH values decreases the hydrogen ion concentration (equation 3.3) in which the hydrogen evolution reactions decreases (cathodic currents) and hence the anodic currents (equation 3.22)

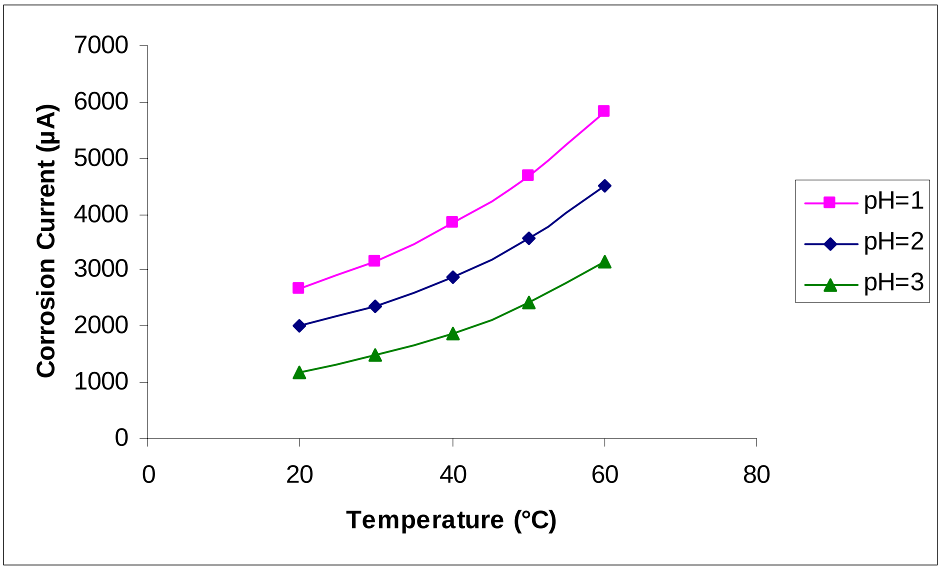

Figure 5.10 Corrosion current of anodic reaction of zinc for system 1 at different temperatures and pH values

Figure 5.11 shows the effect of temperature and pH on the cathodic currents for zinc at system 1, this current is represented by hydrogen evolution on zinc and it is nearly negligible because of the exchange current density for hydrogen evolution is exceedingly small, the curves goes in opposite direction of anodic current because of the minus sign appeared in cathodic current (equation 3.28)

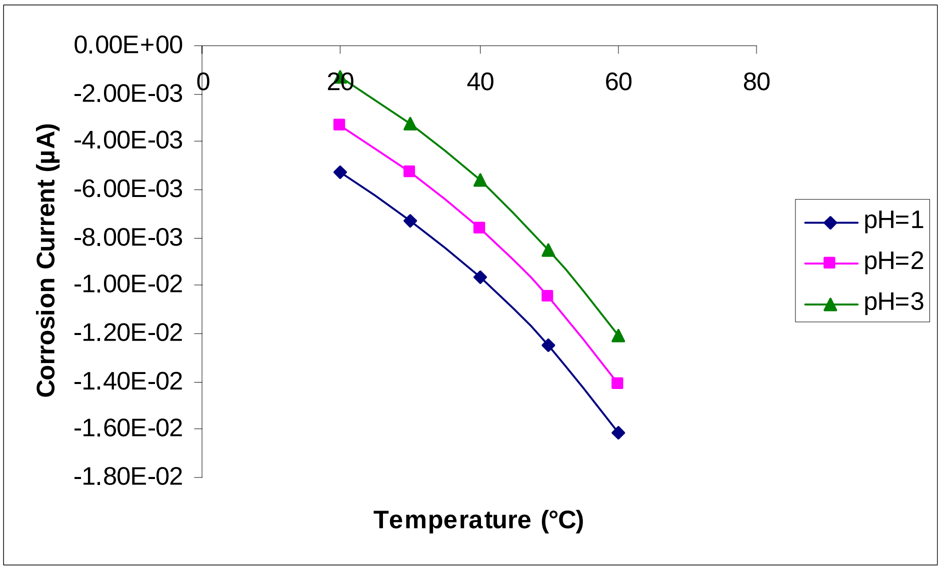

Figure 5.11 The effect of temperature and pH on cathodic reaction on zinc for system 1

Figures 5.12 and 5.13 show the variation of temperature and pH on anodic currents of iron and copper respectively, the values are much smaller than zinc anodic current because they are more positive (noble) than zinc which is more active.

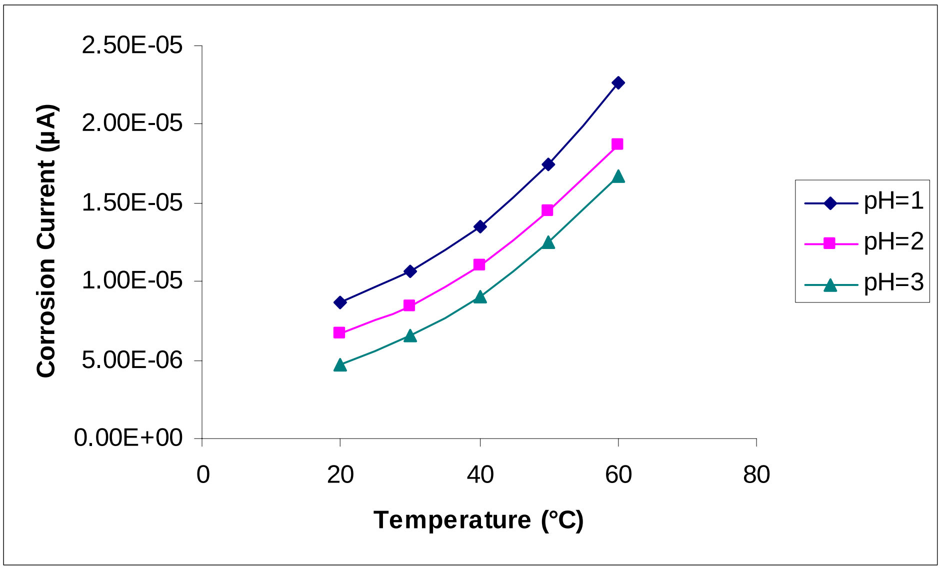

Figure 5.12 The effect of temperature and pH on anodic reaction on iron for system 1

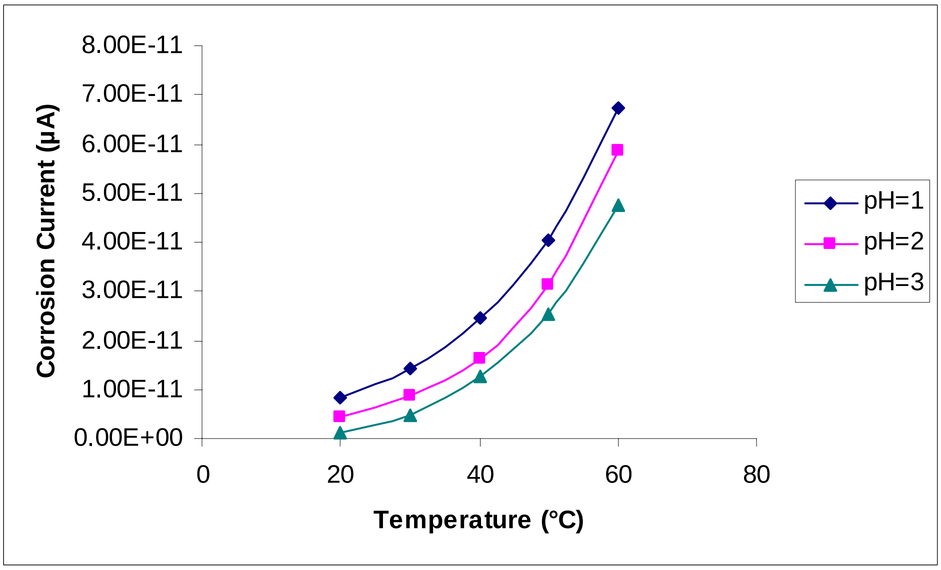

Figure 5.13 The effect of temperature and pH on anodic reaction on copper for system 1

Figure 5.14 gives a clear notation of cathodic current of copper at system 1, in which it is sensible and so greater than its cathodic current because of its great value of hydrogen exchange current density and the positive value of equilibrium potential.

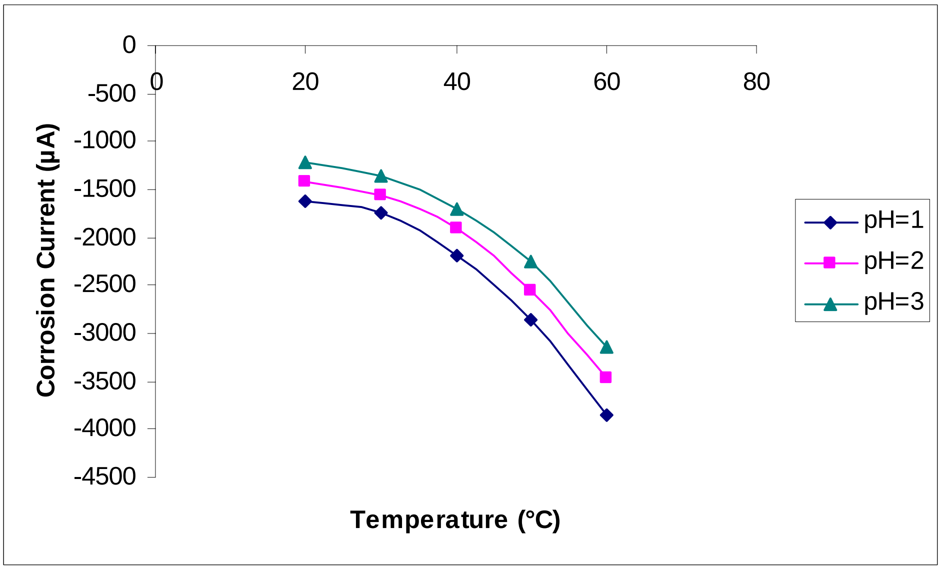

Figure 5.14 The effect of temperature and pH on cathodic reaction on copper for system 1

Figure 5.15 shows the effect of temperature and pH on cathodic reaction of iron which is also sensible but little less than that of copper because of its large value of hydrogen exchange current density but negative value of equilibrium potential.

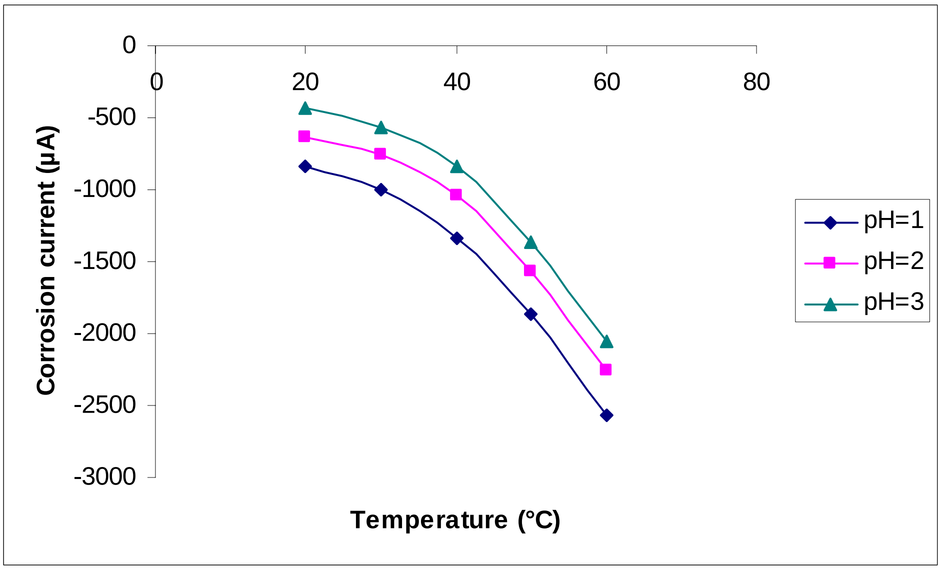

Figure 5.15 The effect of temperature and pH on cathodic reaction on iron for system 1

Figure 5.16 shows all anodic and cathodic currents of system1 at pH=1, it is obvious that zinc acts alone as anodic pole and the cathodic pole divides between copper and iron; therefore, zinc plays as a sacrificial anode and protect both copper and iron. The variation of anodic and cathodic currents with temperature and as in galvanic coupling, separate anodic and cathodic reactions occur; the more active metal (zinc) has the greatest anodic reaction but smallest (nearly negligible) cathodic current because of its smallest value of equilibrium potential and small value of exchange current density for the hydrogen evolution on it. The less active metal (iron) plays a small rule here when posses little anodic and noticeable cathodic currents, the more noble metal (copper) has the smallest anodic reaction and the greatest cathodic reaction.

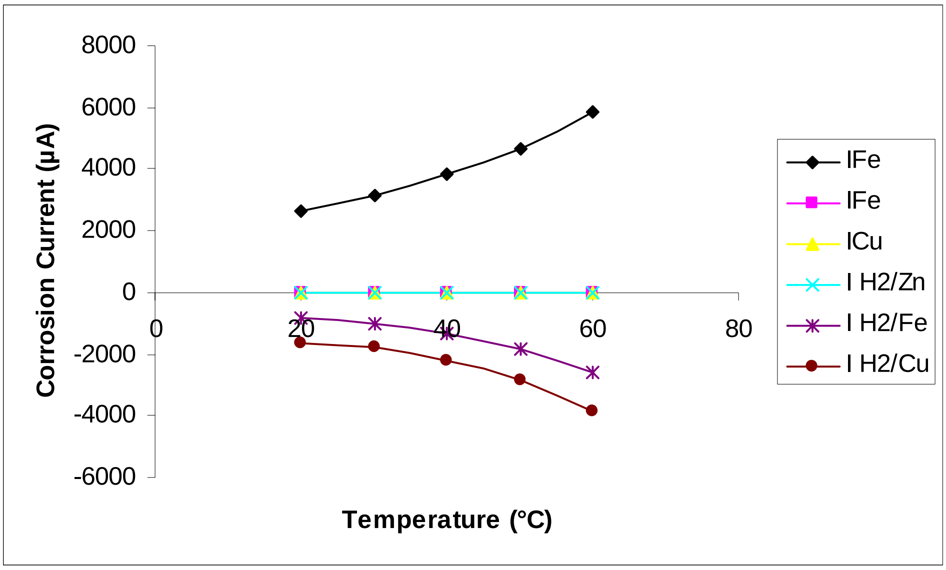

Figure 5.16 The anodic and cathodic corrosion currents for system 1 at different temperatures and at pH=1

Figures 5.17 and 5.18 illustrate the effect of area fractions on corrosion potential and corrosion current respectively. As in galvanic coupling, when the area fraction of cathode is greater than that of the anode the corrosion potential is shifting towards nobility (more noble, i.e. less negative side) at the same time the corrosion current decreased, by the way the corrosion rate increased. Because of iron and copper act as cathode together the summation of their area fractions plays as the area fraction of the cathode and the area fraction of zinc alone is of the anode.

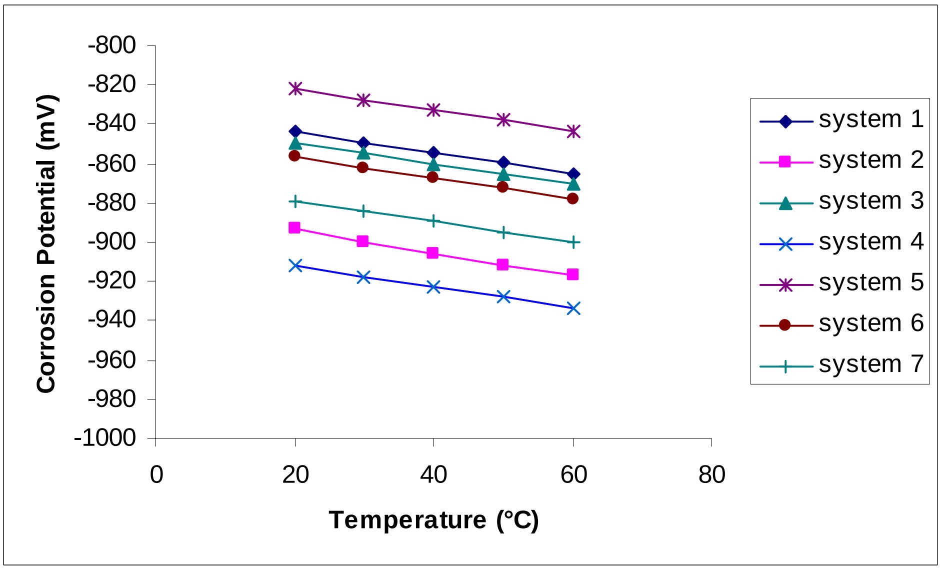

Figure 5.17 The effect of area fractions on the corrosion potential of ternary galvanic systems at pH=1

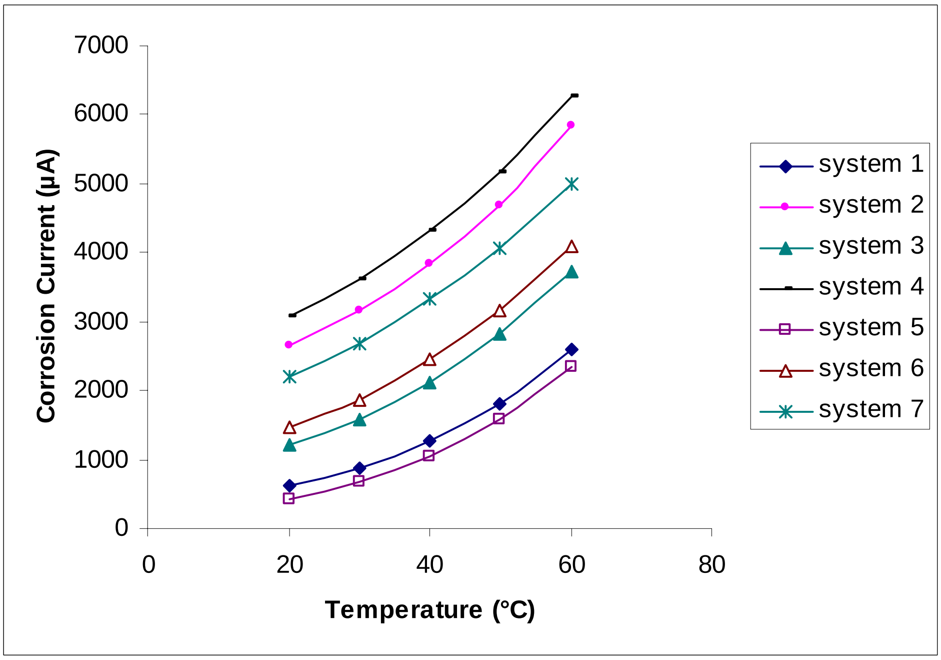

Figure 5.18 The effect of area fractions on the anodic corrosion current of zinc for ternary galvanic systems at pH=1

From figs 5.17 and 5.18 the systems can be rearranged according to anodic and cathodic area ratios as follows:

1. System 4 posses the greatest current amount but the lowest potential value; the area fraction of zinc (anode) is the maximum (0.8) and the cathodic materials (copper=0.1) and (iron=0.1) so the area fractions of the cathode at minimum.
2. System 2 has less current than system 4 and higher potential; area fractions of zinc=0.5,copper0.1 and iron=0.4
3. System 7 has less current than system 2 and higher potential; area fractions of zinc=0.4, copper=0.5 and iron =0.1. The copper is more cathodic than iron so it shifts the potential to more nobility and the corrosion rate increased.
4. System 6 has less current than system 7 and higher potential due to area fractions of zinc=0.1, copper=0.4, iron=0.5
5. System 3 shows a decrease in current, and an increase in potential and another increase in corrosion rate that because the area fraction which is distributed as follows: zinc=0.1, copper=0.5, iron=0.4. The copper is more noble than iron and its area fraction is higher than that of system 6.
6. System 1 shows another decrease in current, and other increase in potential and an increased corrosion rate, due to area fractions of: zinc=0.1, copper=0.1, iron=0.8.

7. System 5 has the maximum amount of corrosion potential and corrosion rate, but the minimum corrosion current; all of this is because of area fraction of zinc=0.1, copper=0.8 and iron=0.1.

CHAPTER SIX

Conclusions and Recommendation for Future works

6.1 Conclusions :

1- The corrosion potential decreases and corrosion current increases when temperature increases at constant pH value for free corrosion, binary and ternary galvanic systems.

2- When pH value increases, the corrosion potential increases (shifts to more positive side) and corrosion current decreases.

3- In binary galvanic corrosion, when area ratio of cathode to anode increases the corrosion potential increases but the corrosion current decreases. At the same time in ternary galvanic corrosion, when area fraction of the more noble metal (copper) increases, the corrosion potential increases while the corrosion current decreases.

4- In ternary system at particular area fractions, the highest currents are that of more active metal (zinc) as it behaves as an anode while iron and copper behave as cathode.

5- In ternary system, increasing area fraction of more noble metal shifts the corrosion potential to more positive values leading to decrease the hydrogen reduction currents on metals and to decrease the zinc corrosion current, leading to increase the galvanic cell corrosion current.

6- For systems of high more noble metal (copper) area fraction, the hydrogen evolution currents are lower than that of high area fractions of more active metal (zinc), leading to increase the corrosion rates.

7- In ternary system, increasing the area fraction of iron shifts the corrosion potential to more positive and decrease the zinc corrosion currents.

6.2 Recommendation for Future Works :

1- Application the present work experimentally.

2- Use other metals like alumenium, magnesium and lead.

3- Performing the analysis for wider range of temperature, pH and area fractions.

4- Investigation of the effect of oxygen (aerated system).

5- Investigation of the effect of velocity on the corrosion rate and corrosion potential in aerated system.

6- Replacing the present electrolyte by another solution.

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Appendix A

Metals' Properties

A.1 Activation energy [4]:

metal	Activation energy (KJ/Kg)
Cu	13609
Zn	2825
Fe	40000

A.2 Electrical Properties [1, 9, 10, 11]:

metal	$i_0(A/m^2)$	$i_{0H}(A/m^2)$	E^o (V)
Cu	0.2	2*10^-3	0.337
Zn	0.3	1.6*10^-7	-0.763
Fe	10^-4	0.0125	-0.44

Appendix B

PROGRAM

```
REM=free corr. Zn
T = 30 + 273: R = 8.314: F = 96487: pH = .7: z = 2
Iozn = .3: Iohzn = 1.6 * 10 ^ -7
A = 1: Ea = 13609
Pt = 101.1: ch = .2
EoZn = -.763
I = .01
IoZn1 = IoZn * ch / A
IohZn1 = IohZn * ch / A
Eg = -.4
FOR J = 1 TO 3
EH = -(R * T / F) * (LOG(1 / ch))
EQZn = EoZn - ((R * T / (z * F)) * LOG(1 / I))
IoZn2 = IoZn1 * EXP((Ea / R) * (1 / 298 - 1 / T))
IohZn2 = IohZn1 * EXP((Ea / R) * (1 / 298 - 1 / T))
50 IZn = IoZn2 * EXP((.5 * F * z) / (R * T) * (Eg - EQZn))
IcZn = IohZn2 * EXP(((-.5 * F) / (R * T)) * (Eg - EH))
IF ABS(IZn - IcZn) <= .000001 THEN 100
Eg = Eg - .0000001#
'PRINT Eg, EH, EQZn; IcZn; IZn; T
GOTO 50
```

```
100 PRINT "Ecorr", "EH", "EQZn", "IcZn", "IZn", "T"
PRINT Eg, EH, EQZn, IcZn, IZn, T
T = T + 15
NEXT
PRINT "_______________________________________________________"
END
```

****

****

```
REM=free corr. Fe
T = 15 + 273: R = 8.314: F = 96487: pH = .7: z = 2
IoFe = 10 ^ -4: IohFe = .0125
A = 1: Ea = 40000: Ec = 30000
Pt = 101.1: ch = .2
EoFe = -.44
I = .0001
IoFe1 = IoFe * ch / A
IohFe1 = IoFe * ch / A
Eg = -.1
FOR J = 1 TO 3
T = T + 15
EH = -(R * T / F) * (LOG(1 / ch))
EQFe = EoFe - ((R * T / (z * F)) * LOG(1 / I))
```

```
IoFe2 = IoFe1 * EXP((Ea / R) * (1 / 298 - 1 / T))

IohFe2 = IohFe1 * EXP((Ec / R) * (1 / 298 - 1 / T))

50 IFe = IoFe2 * EXP(((.5 * F * z) / (R * T)) * (Eg - EQFe))

IcFe = IohFe2 * EXP(((-.5 * F * 1) / (R * T)) * (Eg - EH))

IF ABS(IFe - IcFe) <= .001 THEN 100

Eg = Eg - .001

GOTO 50

100 PRINT "Ecorr", "EH", "EQFe", "IcFe", "IFe", "T"

PRINT Eg, EH, EQFe, IcFe, IFe, T

NEXT

PRINT "--------------------------------"

END
```

```
**************************************************

***********

REM=free corr. Cu

REM:effect of temp.

T = 30 + 273: R = 8.314: F = 96487: pH = .7: z = 2

IoCu = .2: IohCu = 2 * 10 ^ -3

A = 1: Ea = 29760

Pt = 101.1: ch = .2

EoCu = .337

I = .0001
```

```
IoCu1 = IoCu * ch / A

IohCu1 = IohCu * ch / A

FOR J = 1 TO 3

EH = -(R * T / F) * (LOG(1 / ch))

EQCu = EoCu - ((R * T / (z * F)) * LOG(1 / I))

IoCu2 = IoCu1 * EXP((Ea / R) * (1 / 298 - 1 / T))

IohCu2 = IohCu1 * EXP((Ea / R) * (1 / 298 - 1 / T))

Eg = -1 * ((LOG(Iocu) - LOG(IohCu) - ((2 * F * z) / (R * T) * (.5 * E

ICu = IoCu2 * EXP((.5 * F * z / (R * T)) * (Eg - EQCu))

IcCu = IohCu2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

PRINT "Ecorr", "EH", "EQcu", "IcCu", "ICu"

PRINT Eg, EH, EQCu, IcCu, ICu

T = T + 15

NEXT

END
```

****

****

```
REM=free corr. Zn

T = 20 + 273: R = 8.314: F = 96487: z = 2

IoZn = .3: IohZn = 1.6 * 10 ^ -7

A = 1: Ea = 13609
```

```
Pt = 101.1: ch = .1

EoZn = -.763

'FOR M = 1 TO 3

I = .01

IoZn1 = IoZn * ch / A

IohZn1 = IohZn * ch / A

Eg = -.4

FOR J = 1 TO 5

EH = -(R * T / F) * (LOG(1 / ch))

EQZn = EoZn - ((R * T / (z * F)) * LOG(1 / I))

IoZn2 = IoZn1 * EXP((Ea / R) * (1 / 298 - 1 / T))

IohZn2 = IohZn1 * EXP((Ea / R) * (1 / 298 - 1 / T))

50 IZn = IoZn2 * EXP((.5 * F * z) / (R * T) * (Eg - EQZn))

IcZn = IohZn2 * EXP(((-.5 * F) / (R * T)) * (Eg - EH))

IF ABS(IZn - IcZn) <= .000001 THEN 100

Eg = Eg - .0000001#

'PRINT Eg, EH, EQZn; IcZn; IZn; T

GOTO 50

100 PRINT "Ecorr", "EH", "EQZn", "IcZn", "IZn", "T"

PRINT Eg, EH, EQZn, IcZn, IZn, T

T = T + 10

NEXT

ch = ch * .1
```

```
NEXT M
PRINT "_____________________________________________________"
END
```

```
************************************************
***********

REM=free corr. Fe
 R = 8.314: F = 96487: z = 2
IoFe = 10 ^ -4: IohFe = .0125
A = 1: Ea = 40000: Ec = 30000
Pt = 101.1: ch = .1
EoFe = -.44
I = .0001
'FOR M = 1 TO 3
'PRINT "pH="; M
T = 10 + 273
IoFe1 = IoFe * ch / A
IohFe1 = IoFe * ch / A
Eg = -.1
FOR J = 1 TO 6
T = T + 10
EH = -(R * T / F) * (LOG(1 / ch))
```

```
EQFe = EoFe - ((R * T / (z * F)) * LOG(1 / I))

IoFe2 = IoFe1 * EXP((Ea / R) * (1 / 298 - 1 / T))

IohFe2 = IohFe1 * EXP((Ec / R) * (1 / 298 - 1 / T))

50 IFe = IoFe2 * EXP(((.5 * F * z) / (R * T)) * (Eg - EQFe))

IcFe = IohFe2 * EXP(((-.5 * F * 1) / (R * T)) * (Eg - EH))

IF ABS(IFe - IcFe) <= .001 THEN 100

Eg = Eg - .001

GOTO 50

100 PRINT "Ecorr", "EH", "EQFe", "IcFe", "IFe", "T"

PRINT Eg, EH, EQFe, IcFe, IFe, T

NEXT J

'ch = ch * .1

'NEXT M

PRINT """""""""""""""""

END
```

****

****

```
REM=free corr. Cu

REM=effect of pH ,temp.

T = 20 + 273: R = 8.314: F = 96487: z = 2

IoCu = .2: IohCu = 2 * 10 ^ -3
```

```
A = 1: Ea = 29760
Pt = 101.1: ch = .1
EoCu = .337
I = 1 * 10 ^ -10
PRINT "pH"; J
Eg = -.01
FOR J = 1 TO 3
IoCu1 = IoCu * ch / A
IohCu1 = IohCu * ch / A
FOR I = 1 TO 5
EH = -(R * T / F) * (LOG(1 / ch))
EQCu = EoCu - ((R * T / (z * F)) * LOG(1 / I))
IoCu2 = IoCu1 * EXP((Ea / R) * (1 / 298 - 1 / T))
IohCu2 = IohCu1 * EXP((Ea / R) * (1 / 298 - 1 / T))
50 ICu = IoCu2 * EXP((.5 * F * z) / (R * T) * (Eg - EQCu))
IcCu = IohCu2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
IF ABS(ICu - IcCu) <= .0001 THEN 100
Eg = Eg - .00000001#
GOTO 50
100 PRINT "Ecorr", "EH", "EQCu", "IcCu", "ICu"
PRINT Eg, EH, EQCu, IcCu, ICu
T = T + 10
NEXT I
```

```
ch = ch * .1

NEXT J

PRINT "-----------------------------------"

END
```

****

****

```
REM: T=30 C

T = 30 + 273: R = 8.314: PH = .7: F = 96487: z1 = 2: z2 = 2

IoFe = 10 ^ -4: IoCu = .2: IohFe = .012589: IohCu = .2 * 10 ^ -3

A = 1: f1 = .5: f2 = .5: EaFe = 40000: EcFe = 30000: ECu = 29760

Pt = 101.1: ch = .2

EoFe = -.44: EoCu = .337

IFe = 10 ^ -4

ICu = 10 ^ -10

kk = .00001

tt = .0000001#

IoFe1 = IoFe * ch / A

IoCu1 = IoCu * ch / A

Eg = -.2

FOR J = 1 TO 3

EH = -(R * T) * LOG(1 / ch) / F

EQFe = EoFe - ((R * T / (z1 * F)) * LOG(1 / IFe))
```

```
EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))

100 IoFe2 = IoFe1 * EXP((EaFe / R) * (1 / 298 - 1 / T))

IoCu2 = IoCu1 * EXP((EaCu / R) * (1 / 298 - 1 / T))

IFe = IoFe2 * f1 * EXP(.5 * F * z1 / (R * T) * (Eg - EQFe))

ICu = IoCu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQCu))

Ia = IFe + ICu

IohFe2 = IohFe1 * EXP((EcFe / R) * (1 / 298 - 1 / T))

IohCu2 = IohCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))

IcFe = IohFe2 * f1 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

IcCu = IohCu2 * f2 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

Ic = IcFe + IcCu

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 15

NEXT

PRINT "________________________"

END
```

```
**************************************************

***********

ICu = 10 ^ -10
```

```
kk = .00001

tt = .0000001#

IoFe1 = IoFe * ch / A

IoCu1 = IoCu * ch / A

Eg = -.2

FOR J = 1 TO 3

EH = -(R * T) * LOG(1 / ch) / F

EQFe = EoFe - ((R * T / (z1 * F)) * LOG(1 / IFe))

EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))

100 IoFe2 = IoFe1 * EXP((EaFe / R) * (1 / 298 - 1 / T))

IoCu2 = IoCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))

IFe = IoFe2 * f1 * EXP(.5 * F * z1 / (R * T) * (Eg - EQFe))

ICu = IoCu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQCu))

Ia = IFe + ICu

IohFe2 = IohFe1 * EXP((EcFe / R) * (1 / 298 - 1 / T))

IohCu2 = IohCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))

IcFe = IohFe2 * f1 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

IcCu = IohCu2 * f2 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

Ic = IcFe + IcCu

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100
```

```
200 PRINT "Eg", "Ia", "Ic", "T"
PRINT Eg, Ia, Ic, T
T = T + 15
NEXT
PRINT "________________________"
END
```

****

```
Icu = 10 ^ -10
kk = .00001
tt = .0000001#
IoFe1 = IoFe * ch / A
IoCu1 = IoCu * ch / A
Eg = -.2
FOR J = 1 TO 3
EH = -(R * T) * LOG(1 / ch) / F
EQFe = EoFe - ((R * T / (z1 * F)) * LOG(1 / IFe))
EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))
100 IoFe2 = IoFe1 * EXP((EaFe / R) * (1 / 298 - 1 / T))
IoCu2 = IoCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
IFe = IoFe2 * f1 * EXP(.5 * F * z1 / (R * T) * (Eg - EQFe))
ICu = IoCu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQCu))
Ia = IFe + ICu
```

```
IohFe2 = IohFe1 * EXP((EcFe / R) * (1 / 298 - 1 / T))

IohCu2 = IohCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))

IcFe = IohFe2 * f1 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

IcCu = IohCu2 * f2 * EXP((-.5 * F * 1) * (Eg - EH) / (R * T))

Ic = IcFe + IcCu

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 15

NEXT

PRINT "________________________"

END
```

****

****

```
T = 30 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2

IoZn = .3: IoCu = .2: Iohzn = 1.6 * 10 ^ -7: IohCu = 2 * 10 ^ -3

A = 1: f1 = .5: f2 = .5: EZn = 13609: ECu = 29760

Pt = 101.1: ch = .2

EoZn = -.763: EoCu = .337
```

```
IZn = 10 ^ -2
ICu = 10 ^ -10
kk = .00001
tt = .0000001#
IoZn1 = IoZn * ch / A
IoCu1 = IoCu * ch / A
IohZn1 = IohZn * ch / A
IohCu1 = IohCu * ch / A
Eg = -.2
FOR J = 1 TO 3
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQZn = EoZn - ((R * T / (z1 * F)) * LOG(1 / IZn))
EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))
Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
IoCu2 = IoCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
IZn = IoZn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQZn))
ICu = IoCu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQCu))
Ia = IZn + ICu
IohZn2 = IohZn1 * EXP((EZn / R) * (1 / 298 - 1 / T))
IohCu2 = IohCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
IcZn = IohZn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
IcCu = IohCu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = IcZn + IcCu
```

```
RR = ABS(Ia - Ic)
IF RR < kk THEN 200
Eg = Eg - .0000001#
GOTO 100
'IF RR > .0001 THEN Eg = Eg - 100 * tt
  'IF RR > .0001 THEN 300
200 PRINT "Eg", "Ia", "Ic", "T"
PRINT Eg, Ia, Ic, T
T = T + 15
NEXT J
PRINT "______________________________________"
END
```

****
****

```
T = 30 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
IoZn = .3: IoCu = .2: IohZn = 1.6 * 10 ^ -7: IohCu = 2 * 10 ^ -3
A = 1: f1 = 1 / 3: f2 = 2 / 3: EZn = 13609: ECu = 29760
Pt = 101.1: ch = .2
EoZn = -.763: EoCu = .337
IZn = 10 ^ -2
ICu = 10 ^ -10
kk = .00001
```

```
tt = .0000001#
IoZn1 = IoZn * ch / A
IoCu1 = IoCu * ch / A
IohZn1 = IohZn * ch / A
IohCu1 = IohCu * ch / A
Eg = -.2
FOR J = 1 TO 3
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQZn = EoZn - ((R * T / (z1 * F)) * LOG(1 / IZn))
EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))
IoZn2 = IoZn1 * EXP((EZn / R) * (1 / 298 - 1 / T))
IoCu2 = IoCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
IZn = IoZn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQZn))
ICu = IoCu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQCu))
Ia = IZn + ICu
IohZn2 = IohZn1 * EXP((EZn / R) * (1 / 298 - 1 / T))
IohCu2 = IohCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
IcZn = IohZn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
IcCu = IohCu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = IcZn + IcCu
RR = ABS(Ia - Ic)
IF RR < kk THEN 200
Eg = Eg - .0000001#
```

```
GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 15

NEXT J

PRINT "_______________________________________"

END


T = 30 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2

IoZn = .3: IoCu = .2: IohZn = 1.6 * 10 ^ -7: IohCu = 2 * 10 ^ -3

A = 1: f1 = 2 / 3: f2 = 1 / 3: EZn = 13609: ECu = 29760

Pt = 101.1: ch = .2

EoZn = -.763: EoCu = .337

IZn = 10 ^ -2

ICu = 10 ^ -10

kk = .00001

tt = .0000001#

IoZn1 = IoZn * ch / A

IoCu1 = IoCu * ch / A

IohZn1 = IohZn * ch / A

IohCu1 = IohCu * ch / A
```

```
Eg = -.2
FOR J = 1 TO 3 |
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQZn = EoZn - ((R * T / (z1 * F)) * LOG(1 / IZn))
EQCu = EoCu - ((R * T / (z2 * F)) * LOG(1 / ICu))
IoZn2 = IoZn1 * EXP((EZn / R) * (1 / 298 - 1 / T))
IoCu2 = IoCu1 * EXP((ECu / R) * (1 / 298 - 1 / T))
Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))
Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))
Ia = Izn + Icu
Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = Iczn + Iccu
RR = ABS(Ia - Ic)
IF RR < kk THEN 200
Eg = Eg - .0000001#
GOTO 100
'IF RR > .0001 THEN Eg = Eg - 100 * tt
'IF RR > .0001 THEN 300
200 PRINT "Eg", "Ia", "Ic", "T"
PRINT Eg,
```

```
 Ia, Ic, T
T = T + 15
NEXT J
PRINT "_______________________________________"
END
*************************************************************************
**************
   |
T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2
A = 1: f1 = .1: f2 = .1: f3 = .8:
Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000
Pt = 101.1: ch = .1
Eozn = -.763: Eocu = .337: Eofe = -.44
Izn = 10 ^ -2
Icu = 10 ^ -10
Ife = 10 ^ -4
kk = .00001
tt = .0000001#
Iozn1 = Iozn * ch / A
Iocu1 = Iocu * ch / A
Iofe1 = Iofe * ch / A
Iohzn1 = Iohzn * ch / A
```

```
Iohcu1 = Iohcu * ch / A

Iohfe1 = Iohfe * ch / A

Eg = -.2

FOR M = 1 TO 3

T = 20 + 273

PRINT "PH="; M

FOR J = 1 TO 5

100 EH = -(R * T) / (LOG(1 / ch)) * F

EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))

EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))

EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))

Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))

Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQzn))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQcu))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg -
EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
```

```
Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = Iczn + Iccu + Icfe
RR = ABS(Ia - Ic)
IF RR < kk THEN 200
Eg = Eg - .0000001#
GOTO 100
'IF RR > .0001 THEN Eg = Eg - 100 * tt
'IF RR > .0001 THEN 300
200 PRINT "Eg", "Ia", "Ic", "T"
PRINT Eg, Ia, Ic, T
T = T + 10
NEXT J
ch = ch * .1
NEXT M
PRINT "__________________________________________"
END
```

```
 T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^
```

```
A = 1: f1 = .5: f2 = .1: f3 = .4

Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000

Pt = 101.1: ch = .1

Eozn = -.763: Eocu = .337: Eofe = -.44

Izn = 10 ^ -2

Icu = 10 ^ -10

Ife = 10 ^ -4

kk = .00001

tt = .0000001#

Iozn1 = Iozn * ch / A

Iocu1 = Iocu * ch / A

Iofe1 = Iofe * ch / A

Iohzn1 = Iohzn * ch / A

Iohcu1 = Iohcu * ch / A

Iohfe1 = Iohfe * ch / A

Eg = -.2

FOR M = 1 TO 3

T = 20 + 273

PRINT "PH="; M

FOR J = 1 TO 5

100 EH = -(R * T) / (LOG(1 / ch)) * F

EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))

EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))
```

```
EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))

Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))

Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg - EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Ic = Iczn + Iccu + Icfe

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T
```

```
T = T + 10

NEXT J

ch = ch * .1

NEXT M

PRINT "________________________________________"

END
```

```
T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2

Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^

A = 1: f1 = .1: f2 = .5: f3 = .4

Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000

Pt = 101.1: ch = .1

Eozn = -.763: Eocu = .337: Eofe = -.44

Izn = 10 ^ -2

Icu = 10 ^ -10

Ife = 10 ^ -4

kk = .00001

tt = .0000001#

Iozn1 = Iozn * ch / A

Iocu1 = Iocu * ch / A

Iofe1 = Iofe * ch / A

Iohzn1 = Iohzn * ch / A
```

```
Iohcu1 = Iohcu * ch / A
Iohfe1 = Iohfe * ch / A
Eg = -.2
FOR M = 1 TO 3
T = 20 + 273
PRINT "PH="; M
FOR J = 1 TO 5
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))
EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))
EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))
Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))
Ia = Izn + Icu + fe
Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))
Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = Iczn + Iccu + Icfe
RR = ABS(Ia - Ic)
```

```
IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 10

NEXT J

ch = ch * .1

NEXT M

PRINT "________________________________________"

END


Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg -
EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
```

```
Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Ic = Iczn + Iccu + Icfe

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 10

NEXT J

ch = ch * .1

NEXT M

PRINT "________________________________________"

END
```

```
T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2

Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^

A = 1: f1 = .8: f2 = .1: f3 = .1

Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000
```

```
Pt = 101.1: ch = .1
Eozn = -.763: Eocu = .337: Eofe = -.44
Izn = 10 ^ -2
Icu = 10 ^ -10
Ife = 10 ^ -4
kk = .00001
tt = .0000001#
Iozn1 = Iozn * ch / A
Iocu1 = Iocu * ch / A
Iofe1 = Iofe * ch / A
Iohzn1 = Iohzn * ch / A
Iohcu1 = Iohcu * ch / A
Iohfe1 = Iohfe * ch / A

Eg = -.2

FOR M = 1 TO 3
T = 20 + 273
PRINT "PH="; M
FOR J = 1 TO 5
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))
EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))
```

```
EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))

Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))

Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg -
EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Ic = Iczn + Iccu + Icfe

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"
```

```
PRINT Eg, Ia, Ic, T
T = T + 10
NEXT J
ch = ch * .1
NEXT M
PRINT "_________________________________"
END

T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^
A = 1: f1 = .1: f2 = .8: f3 = .1
Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000
Pt = 101.1: ch = .1
Eozn = -.763: Eocu = .337: Eofe = -.44
Izn = 10 ^ -2
Icu = 10 ^ -10
Ife = 10 ^ -4
kk = .00001
tt = .0000001#
Iozn1 = Iozn * ch / A
Iocu1 = Iocu * ch / A
Iofe1 = Iofe * ch / A
Iohzn1 = Iohzn * ch / A
```

```
Iohcu1 = Iohcu * ch / A
Iohfe1 = Iohfe * ch / A
Eg = -.2
FOR M = 1 TO 3
T = 20 + 273
PRINT "PH="; M
FOR J = 1 TO 5
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))
EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))
EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))
Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))
Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))
Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))
Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg - EQfe))
T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^
A = 1: f1 = .1: f2 = .8: f3 = .1
Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000
Pt = 101.1: ch = .1
Eozn = -.763: Eocu = .337: Eofe = -.44
```

```
Izn = 10 ^ -2

Icu = 10 ^ -10

Ife = 10 ^ -4

kk = .00001

tt = .0000001#

Iozn1 = Iozn * ch / A

Iocu1 = Iocu * ch / A

Iofe1 = Iofe * ch / A

Iohzn1 = Iohzn * ch / A

Iohcu1 = Iohcu * ch / A

Iohfe1 = Iohfe * ch / A

Eg = -.2

FOR M = 1 TO 3

T = 20 + 273

PRINT "PH="; M

FOR J = 1 TO 5

100 EH = -(R * T) / (LOG(1 / ch)) * F

EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))

EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))

EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))

Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))
```

```
Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg - EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Ic = Iczn + Iccu + Icfe

RR = ABS(Ia - Ic)

IF RR < kk THEN 200

Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 10

NEXT J

ch = ch * .1

NEXT M
```

```
PRINT "___________________________________________"
END

T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2
Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^
A = 1: f1 = .4: f2 = .1: f3 = .5
Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000
Pt = 101.1: ch = .1
Eozn = -.763: Eocu = .337: Eofe = -.44
Izn = 10 ^ -2
Icu = 10 ^ -10
Ife = 10 ^ -4
kk = .00001
tt = .0000001#
Iozn1 = Iozn * ch / A
Iocu1 = Iocu * ch / A
Iofe1 = Iofe * ch / A
Iohzn1 = Iohzn * ch / A
Iohcu1 = Iohcu * ch / A
Iohfe1 = Iohfe * ch / A
Eg = -.2
FOR M = 1 TO 3
```

```
T = 20 + 273

PRINT "PH="; M

FOR J = 1 TO 5

100 EH = -(R * T) / (LOG(1 / ch)) * F

EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))

EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))

EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))

Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))

Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))

Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))

Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg - EQfe))

Ia = Izn + Icu + fe

Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))

Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))

Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))

Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))

Ic = Iczn + Iccu + Icfe

RR = ABS(Ia - Ic)

IF RR < kk THEN 200
```

```
Eg = Eg - .0000001#

GOTO 100

'IF RR > .0001 THEN Eg = Eg - 100 * tt

'IF RR > .0001 THEN 300

200 PRINT "Eg", "Ia", "Ic", "T"

PRINT Eg, Ia, Ic, T

T = T + 10

NEXT J

ch = ch * .1

NEXT M

PRINT "________________________________________"

END
```

```
T = 20 + 273: R = 8.314: F = 96487: PH = .7: z1 = 2: z2 = 2

Iozn = .3: Iocu = .2: Iofe = 10 ^ -4: Iohzn = 1.6 * 10 ^ -7: Iohcu = 2 * 10 ^

A = 1: f1 = .1: f2 = .4: f3 = .5

Ezn = 13609: Ecu = 29760: Eafe = 40000: Ecfe = 30000

Pt = 101.1: ch = .1

Eozn = -.763: Eocu = .337: Eofe = -.44

Izn = 10 ^ -2

Icu = 10 ^ -10

Ife = 10 ^ -4
```

```
kk = .00001
tt = .0000001#
Iozn1 = Iozn * ch / A
Iocu1 = Iocu * ch / A
Iofe1 = Iofe * ch / A
Iohzn1 = Iohzn * ch / A
Iohcu1 = Iohcu * ch / A
Iohfe1 = Iohfe * ch / A
Eg = -.2
FOR M = 1 TO 3
T = 20 + 273
PRINT "PH="; M
FOR J = 1 TO 5
100 EH = -(R * T) / (LOG(1 / ch)) * F
EQzn = Eozn - ((R * T / (z1 * F)) * LOG(1 / Izn))
EQcu = Eocu - ((R * T / (z2 * F)) * LOG(1 / Icu))
EQfe = Eofe - ((R * T / (z2 * F)) * LOG(1 / Ife))
Iozn2 = Iozn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iocu2 = Iocu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iofe2 = Iofe1 * EXP((Eafe / R) * (1 / 298 - 1 / T))
Izn = Iozn2 * f1 * EXP((.5 * F * z1) / (R * T) * (Eg - EQfe))
Icu = Iocu2 * f2 * EXP(.5 * F * z1 / (R * T) * (Eg - EQzn))
```

```
Ife = Iofe2 * f3 * EXP(.5 * F * z1 / (R * T) * (Eg -
EQfe))


Ia = Izn + Icu + fe
Iohzn2 = Iohzn1 * EXP((Ezn / R) * (1 / 298 - 1 / T))
Iohcu2 = Iohcu1 * EXP((Ecu / R) * (1 / 298 - 1 / T))
Iohfe2 = Iohfe1 * EXP((Ecfe / R) * (1 / 298 - 1 / T))
Iczn = Iohzn2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Iccu = Iohcu2 * f2 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Icfe = Iohfe2 * f1 * EXP((-.5 * F * 1) / (R * T) * (Eg - EH))
Ic = Iczn + Iccu + Icfe
RR = ABS(Ia - Ic)
IF RR < kk THEN 200
Eg = Eg - .0000001#
GOTO 100
'IF RR > .0001 THEN Eg = Eg - 100 * tt
'IF RR > .0001 THEN 300
200 PRINT "Eg", "Ia", "Ic", "T"
PRINT Eg, Ia, Ic, T
T = T + 10
NEXT J
ch = ch * .1
NEXT M
```

```
PRINT "_______________________________________"
END
```

Appendix C
Tables of Exchange Current Density and Tafel Constant for Hydrogen Evolution on Metals

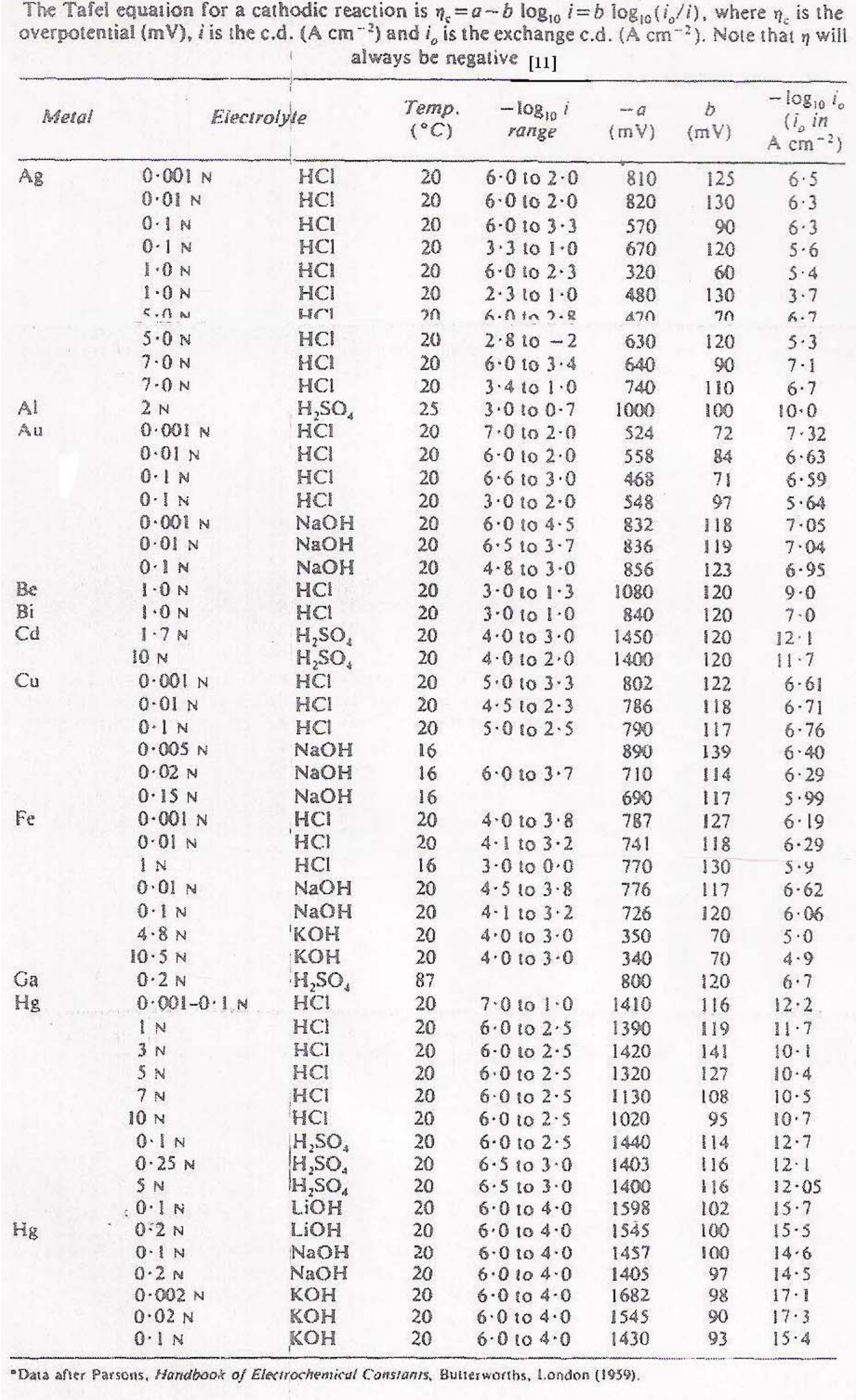


Table 21.12 Tafel constants for hydrogen evolution from aqueous solution*

The Tafel equation for a cathodic reaction is $\eta_c = a - b \log_{10} i = b \log_{10}(i_o/i)$, where η_c is the overpotential (mV), i is the c.d. (A cm^{-2}) and i_o is the exchange c.d. (A cm^{-2}). Note that η will always be negative [11]

Metal	*Electrolyte*		*Temp.* (°C)	$-\log_{10} i$ *range*	$-a$ (mV)	b (mV)	$-\log_{10} i_o$ (i_o *in* A cm^{-2})
Ag	0·001 N	HCl	20	6·0 to 2·0	810	125	6·5
	0·01 N	HCl	20	6·0 to 2·0	820	130	6·3
	0·1 N	HCl	20	6·0 to 3·3	570	90	6·3
	0·1 N	HCl	20	3·3 to 1·0	670	120	5·6
	1·0 N	HCl	20	6·0 to 2·3	320	60	5·4
	1·0 N	HCl	20	2·3 to 1·0	480	130	3·7
	5·0 N	HCl	20	6·0 to 2·8	470	70	6·7
	5·0 N	HCl	20	2·8 to −2	630	120	5·3
	7·0 N	HCl	20	6·0 to 3·4	640	90	7·1
	7·0 N	HCl	20	3·4 to 1·0	740	110	6·7
Al	2 N	H_2SO_4	25	3·0 to 0·7	1000	100	10·0
Au	0·001 N	HCl	20	7·0 to 2·0	524	72	7·32
	0·01 N	HCl	20	6·0 to 2·0	558	84	6·63
	0·1 N	HCl	20	6·6 to 3·0	468	71	6·59
	0·1 N	HCl	20	3·0 to 2·0	548	97	5·64
	0·001 N	NaOH	20	6·0 to 4·5	832	118	7·05
	0·01 N	NaOH	20	6·5 to 3·7	836	119	7·04
	0·1 N	NaOH	20	4·8 to 3·0	856	123	6·95
Be	1·0 N	HCl	20	3·0 to 1·3	1080	120	9·0
Bi	1·0 N	HCl	20	3·0 to 1·0	840	120	7·0
Cd	1·7 N	H_2SO_4	20	4·0 to 3·0	1450	120	12·1
	10 N	H_2SO_4	20	4·0 to 2·0	1400	120	11·7
Cu	0·001 N	HCl	20	5·0 to 3·3	802	122	6·61
	0·01 N	HCl	20	4·5 to 2·3	786	118	6·71
	0·1 N	HCl	20	5·0 to 2·5	790	117	6·76
	0·005 N	NaOH	16		890	139	6·40
	0·02 N	NaOH	16	6·0 to 3·7	710	114	6·29
	0·15 N	NaOH	16		690	117	5·99
Fe	0·001 N	HCl	20	4·0 to 3·8	787	127	6·19
	0·01 N	HCl	20	4·1 to 3·2	741	118	6·29
	1 N	HCl	16	3·0 to 0·0	770	130	5·9
	0·01 N	NaOH	20	4·5 to 3·8	776	117	6·62
	0·1 N	NaOH	20	4·1 to 3·2	726	120	6·06
	4·8 N	KOH	20	4·0 to 3·0	350	70	5·0
	10·5 N	KOH	20	4·0 to 3·0	340	70	4·9
Ga	0·2 N	H_2SO_4	87		800	120	6·7
Hg	0·001–0·1 N	HCl	20	7·0 to 1·0	1410	116	12·2
	1 N	HCl	20	6·0 to 2·5	1390	119	11·7
	3 N	HCl	20	6·0 to 2·5	1420	141	10·1
	5 N	HCl	20	6·0 to 2·5	1320	127	10·4
	7 N	HCl	20	6·0 to 2·5	1130	108	10·5
	10 N	HCl	20	6·0 to 2·5	1020	95	10·7
	0·1 N	H_2SO_4	20	6·0 to 2·5	1440	114	12·7
	0·25 N	H_2SO_4	20	6·5 to 3·0	1403	116	12·1
	5 N	H_2SO_4	20	6·5 to 3·0	1400	116	12·05
	0·1 N	LiOH	20	6·0 to 4·0	1598	102	15·7
Hg	0·2 N	LiOH	20	6·0 to 4·0	1545	100	15·5
	0·1 N	NaOH	20	6·0 to 4·0	1457	100	14·6
	0·2 N	NaOH	20	6·0 to 4·0	1405	97	14·5
	0·002 N	KOH	20	6·0 to 4·0	1682	98	17·1
	0·02 N	KOH	20	6·0 to 4·0	1545	90	17·3
	0·1 N	KOH	20	6·0 to 4·0	1430	93	15·4

*Data after Parsons, *Handbook of Electrochemical Constants*, Butterworths, London (1959).

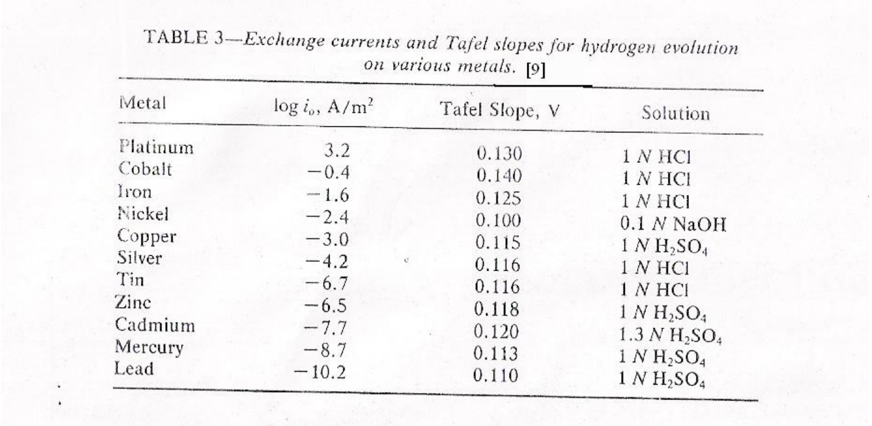


TABLE 3—*Exchange currents and Tafel slopes for hydrogen evolution on various metals.* [9]

Metal	log i_o, A/m^2	Tafel Slope, V	Solution
Platinum	3.2	0.130	1 *N* HCl
Cobalt	−0.4	0.140	1 *N* HCl
Iron	−1.6	0.125	1 *N* HCl
Nickel	−2.4	0.100	0.1 *N* NaOH
Copper	−3.0	0.115	1 *N* H_2SO_4
Silver	−4.2	0.116	1 *N* HCl
Tin	−6.7	0.116	1 *N* HCl
Zinc	−6.5	0.118	1 *N* H_2SO_4
Cadmium	−7.7	0.120	1.3 *N* H_2SO_4
Mercury	−8.7	0.113	1 *N* H_2SO_4
Lead	−10.2	0.110	1 *N* H_2SO_4

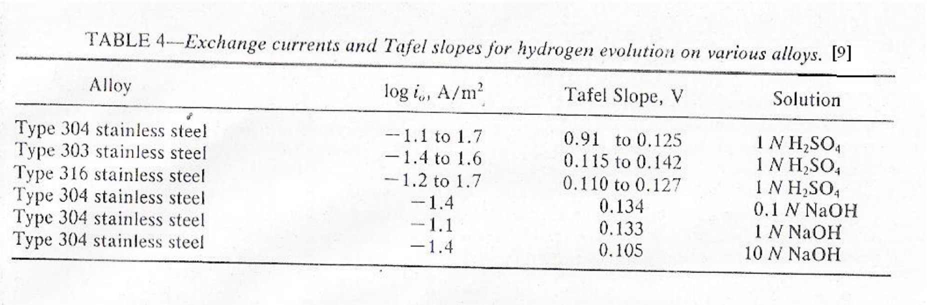


TABLE 4—*Exchange currents and Tafel slopes for hydrogen evolution on various alloys.* [9]

Alloy	log i_o, A/m^2	Tafel Slope, V	Solution
Type 304 stainless steel	−1.1 to 1.7	0.91 to 0.125	1 *N* H_2SO_4
Type 303 stainless steel	−1.4 to 1.6	0.115 to 0.142	1 *N* H_2SO_4
Type 316 stainless steel	−1.2 to 1.7	0.110 to 0.127	1 *N* H_2SO_4
Type 304 stainless steel	−1.4	0.134	0.1 *N* NaOH
Type 304 stainless steel	−1.1	0.133	1 *N* NaOH
Type 304 stainless steel	−1.4	0.105	10 *N* NaOH

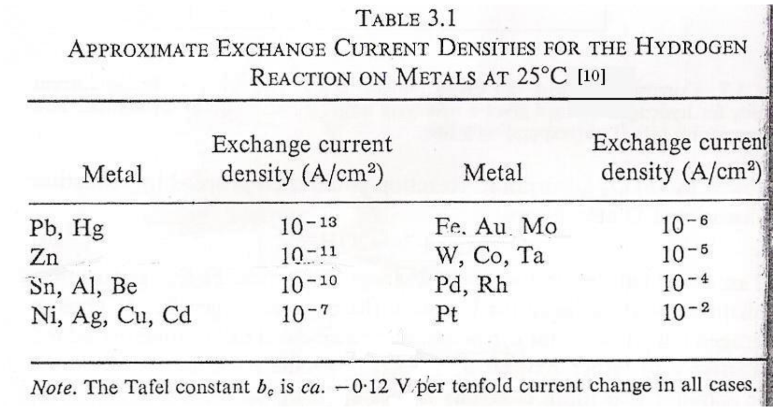
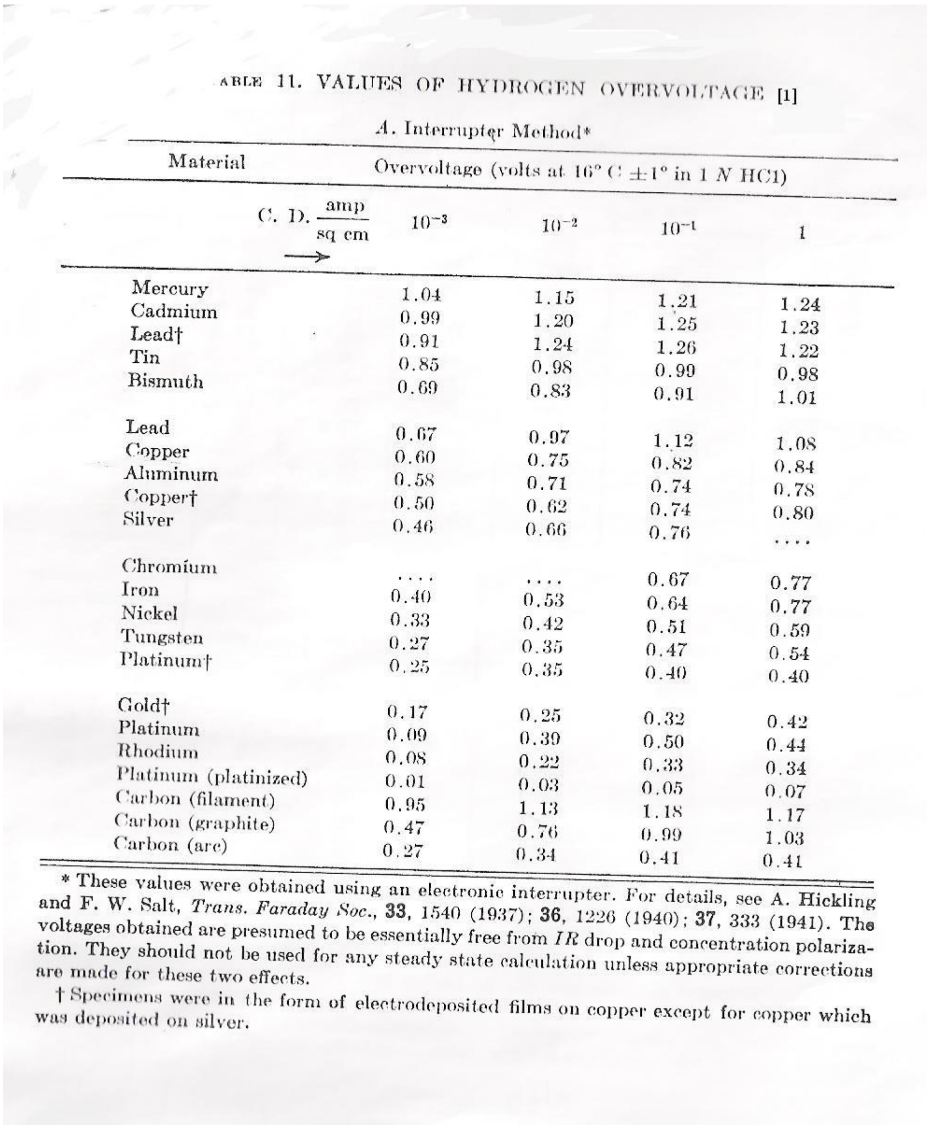


Table 3.1

Approximate Exchange Current Densities for the Hydrogen Reaction on Metals at 25°C [10]

Metal	Exchange current density (A/cm^2)	Metal	Exchange current density (A/cm^2)
Pb, Hg	10^{-13}	Fe, Au, Mo	10^{-6}
Zn	10^{-11}	W, Co, Ta	10^{-5}
Sn, Al, Be	10^{-10}	Pd, Rh	10^{-4}
Ni, Ag, Cu, Cd	10^{-7}	Pt	10^{-2}

Note. The Tafel constant b_c is *ca.* $-0{\cdot}12$ V per tenfold current change in all cases.



ABLE 11. VALUES OF HYDROGEN OVERVOLTAGE [1]

A. Interrupter Method*

Material	Overvoltage (volts at 16° C ±1° in 1 *N* HCl)			
C. D. $\frac{\text{amp}}{\text{sq cm}}$ →	10^{-3}	10^{-2}	10^{-1}	1
Mercury	1.04	1.15	1.21	1.24
Cadmium	0.99	1.20	1.25	1.23
Lead†	0.91	1.24	1.26	1.22
Tin	0.85	0.98	0.99	0.98
Bismuth	0.69	0.83	0.91	1.01
Lead	0.67	0.97	1.12	1.08
Copper	0.60	0.75	0.82	0.84
Aluminum	0.58	0.71	0.74	0.78
Copper†	0.50	0.62	0.74	0.80
Silver	0.46	0.66	0.76	....
Chromium	....	....	0.67	0.77
Iron	0.40	0.53	0.64	0.77
Nickel	0.33	0.42	0.51	0.59
Tungsten	0.27	0.35	0.47	0.54
Platinum†	0.25	0.35	0.40	0.40
Gold†	0.17	0.25	0.32	0.42
Platinum	0.09	0.39	0.50	0.44
Rhodium	0.08	0.22	0.33	0.34
Platinum (platinized)	0.01	0.03	0.05	0.07
Carbon (filament)	0.95	1.13	1.18	1.17
Carbon (graphite)	0.47	0.76	0.99	1.03
Carbon (arc)	0.27	0.34	0.41	0.41

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* These values were obtained using an electronic interrupter. For details, see A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **33**, 1540 (1937); **36**, 1226 (1940); **37**, 333 (1941). The voltages obtained are presumed to be essentially free from *IR* drop and concentration polarization. They should not be used for any steady state calculation unless appropriate corrections are made for these two effects.

† Specimens were in the form of electrodeposited films on copper except for copper which was deposited on silver.

Appendix D

Tables of Exchange Current Density on Metals

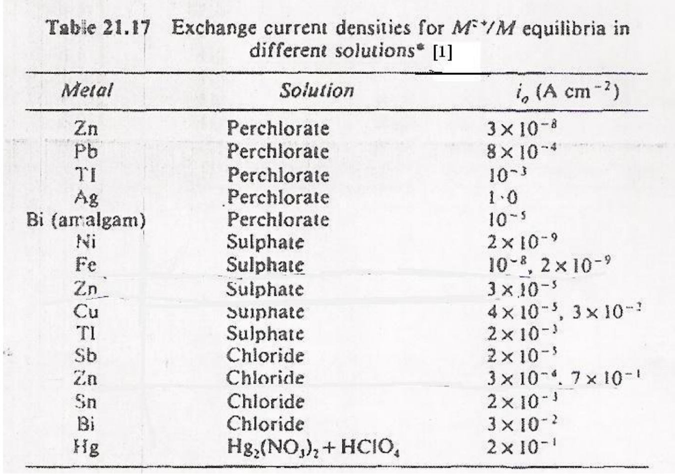

Table 21.17 Exchange current densities for M^{z+}/M equilibria in different solutions* [1]

Metal	*Solution*	i_o (A cm^{-2})
Zn	Perchlorate	3×10^{-8}
Pb	Perchlorate	8×10^{-4}
Tl	Perchlorate	10^{-3}
Ag	Perchlorate	1·0
Bi (amalgam)	Perchlorate	10^{-5}
Ni	Sulphate	2×10^{-9}
Fe	Sulphate	10^{-8}, 2×10^{-9}
Zn	Sulphate	3×10^{-5}
Cu	Sulphate	4×10^{-5}, 3×10^{-2}
Tl	Sulphate	2×10^{-3}
Sb	Chloride	2×10^{-5}
Zn	Chloride	3×10^{-4}, 7×10^{-1}
Sn	Chloride	2×10^{-3}
Bi	Chloride	3×10^{-2}
Hg	$Hg_2(NO_3)_2 + HClO_4$	2×10^{-1}

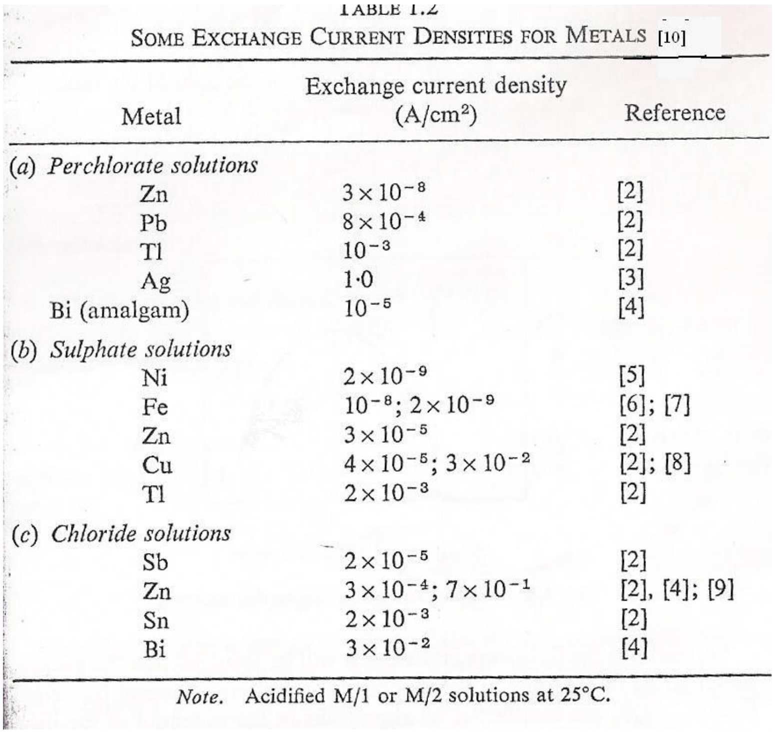

TABLE 1.2

SOME EXCHANGE CURRENT DENSITIES FOR METALS [10]

Metal	Exchange current density (A/cm^2)	Reference
(*a*) *Perchlorate solutions*		
Zn	3×10^{-8}	[2]
Pb	8×10^{-4}	[2]
Tl	10^{-3}	[2]
Ag	1·0	[3]
Bi (amalgam)	10^{-5}	[4]
(*b*) *Sulphate solutions*		
Ni	2×10^{-9}	[5]
Fe	10^{-8}; 2×10^{-9}	[6]; [7]
Zn	3×10^{-5}	[2]
Cu	4×10^{-5}; 3×10^{-2}	[2]; [8]
Tl	2×10^{-3}	[2]
(*c*) *Chloride solutions*		
Sb	2×10^{-5}	[2]
Zn	3×10^{-4}; 7×10^{-1}	[2], [4]; [9]
Sn	2×10^{-3}	[2]
Bi	3×10^{-2}	[4]

Note. Acidified M/1 or M/2 solutions at 25°C.

Appendix E

Sample of Calculations

Down here a sample of calculations for free corrosion of copper at T=30°C and pH=0.7:

$$E_{Cu}^{eq} = 0.337 - [(8.314 * 303)/(2 * 96487) * \ln \frac{1}{10^{-10}}$$

$$E_{Cu}^{eq} = 0.36413453 \quad \text{V}$$

$$[H^+] = 0.2 \quad \text{M}$$

$$E_{H_2}^{eq} = 0.0 - [(8.314 * 303)/(1 * 96487) \ln \frac{1}{0.2}$$

$$E_{H_2}^{eq} = -0.042020195 \quad \text{V}$$

Taken basis of 1 m^2

$$i_{o,Cu1} = 0.2 * 0.2/1 = 0.04 \quad \text{A}$$

$$i_{o,Cu2} = 0.04 * \exp[(29760/8.314) * (\frac{1}{298} - \frac{1}{303})]$$

$i_{o,Cu2}$ =0.048768924 A

$$i_{o,H_2/Cu1} = 2 * 10^{-3} * 0.2/1 = 4 * 10^{-4} \quad \text{A}$$

$$i_{o,H_2/Cu2} = 4 * 10^{-4} * \exp[(29760/8.314) * (\frac{1}{298} - \frac{1}{303})]$$

$i_{o,H_2/Cu2}$ =4.876892435*10^{-4} A

$$I_{Cu} = 0.048768924 * \exp[(0.5 * 96487 * 2)/(8.314 * 303) * (E^{corr} - 0.36413453)\ ] \quad \text{….(1)}$$

$$I_{H_2/Cu} = 4.876892435*10^{-4}*\exp[(-0.5*96487)/(8.314*303)*(E^{corr}-(-0.042020195))$$

…(2)

After many trials of assuming E^{corr} and substituting it in equations (1) and (2), it was found that;

$E^{corr} = -0.07083$ V

$I_{Cu} = 8.0212136*10^{-4}$ A

$I_{H2/Cu} = -8.46752323*10^{-4}$ A

$|I_{Cu} - I_{H_2/Cu}| = 4.463*10^{-5} < 10^{-4}$

Appendix F

Electromotive Force Series

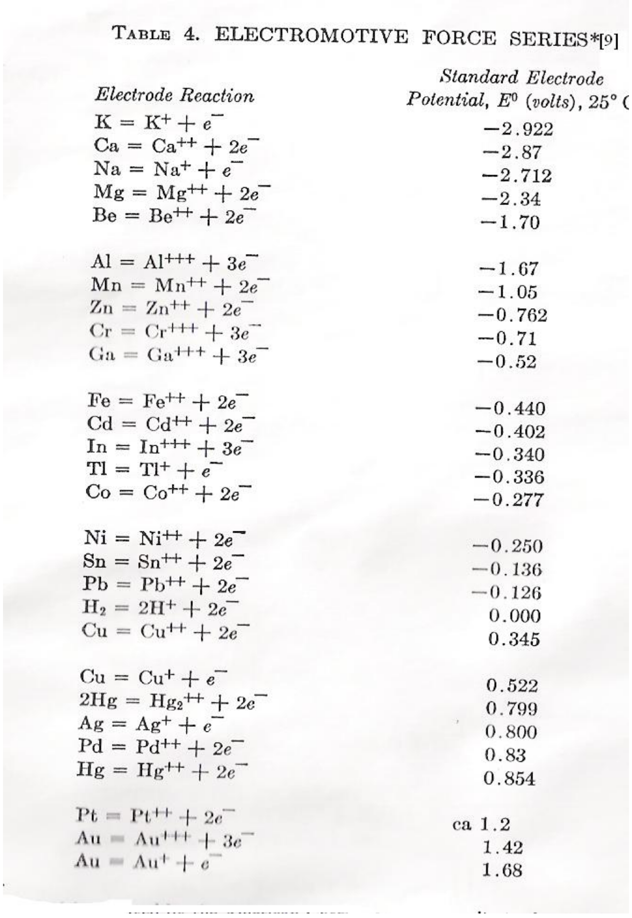

TABLE 4. ELECTROMOTIVE FORCE SERIES*[9]

Electrode Reaction	*Standard Electrode Potential, E^0 (volts), 25° (*
$K = K^+ + e^-$	−2.922
$Ca = Ca^{++} + 2e^-$	−2.87
$Na = Na^+ + e^-$	−2.712
$Mg = Mg^{++} + 2e^-$	−2.34
$Be = Be^{++} + 2e^-$	−1.70
$Al = Al^{+++} + 3e^-$	−1.67
$Mn = Mn^{++} + 2e^-$	−1.05
$Zn = Zn^{++} + 2e^-$	−0.762
$Cr = Cr^{+++} + 3e^-$	−0.71
$Ga = Ga^{+++} + 3e^-$	−0.52
$Fe = Fe^{++} + 2e^-$	−0.440
$Cd = Cd^{++} + 2e^-$	−0.402
$In = In^{+++} + 3e^-$	−0.340
$Tl = Tl^+ + e^-$	−0.336
$Co = Co^{++} + 2e^-$	−0.277
$Ni = Ni^{++} + 2e^-$	−0.250
$Sn = Sn^{++} + 2e^-$	−0.136
$Pb = Pb^{++} + 2e^-$	−0.126
$H_2 = 2H^+ + 2e^-$	0.000
$Cu = Cu^{++} + 2e^-$	0.345
$Cu = Cu^+ + e^-$	0.522
$2Hg = Hg_2^{++} + 2e^-$	0.799
$Ag = Ag^+ + e^-$	0.800
$Pd = Pd^{++} + 2e^-$	0.83
$Hg = Hg^{++} + 2e^-$	0.854
$Pt = Pt^{++} + 2e^-$	ca 1.2
$Au = Au^{+++} + 3e^-$	1.42
$Au = Au^+ + e^-$	1.68

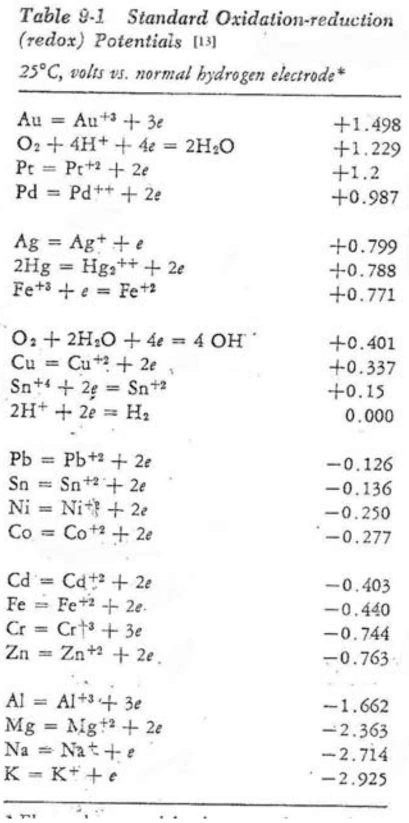

Table 9-1 Standard Oxidation-reduction (redox) Potentials [13]

*25°C, volts vs. normal hydrogen electrode**

$Au = Au^{+3} + 3e$	+1.498
$O_2 + 4H^+ + 4e = 2H_2O$	+1.229
$Pt = Pt^{+2} + 2e$	+1.2
$Pd = Pd^{++} + 2e$	+0.987
$Ag = Ag^+ + e$	+0.799
$2Hg = Hg_2^{++} + 2e$	+0.788
$Fe^{+3} + e = Fe^{+2}$	+0.771
$O_2 + 2H_2O + 4e = 4\ OH^-$	+0.401
$Cu = Cu^{+2} + 2e$	+0.337
$Sn^{+4} + 2e = Sn^{+2}$	+0.15
$2H^+ + 2e = H_2$	0.000
$Pb = Pb^{+2} + 2e$	−0.126
$Sn = Sn^{+2} + 2e$	−0.136
$Ni = Ni^{+2} + 2e$	−0.250
$Co = Co^{+2} + 2e$	−0.277
$Cd = Cd^{+2} + 2e$	−0.403
$Fe = Fe^{+2} + 2e$	−0.440
$Cr = Cr^{+3} + 3e$	−0.744
$Zn = Zn^{+2} + 2e$	−0.763
$Al = Al^{+3} + 3e$	−1.662
$Mg = Mg^{+2} + 2e$	−2.363
$Na = Na^+ + e$	−2.714
$K = K^+ + e$	−2.925

Appendix G
Galvanic Series

The Galvanic Table in Flowing Sea Water [9, 18]:

Active (Anodic)

1. Magnesium
2. Mg alloy AZ-31B
3. Mg alloy HK-31A
4. Zinc (hot-dip, die cast, or plated)
5. Beryllium (hot pressed)
6. Al 7072 clad on 7075
7. Al 2014-T3
8. Al 1160-H14
9. Al 7079-T6
10. Cadmium (plated)
11. Uranium
12. Al 218 (die cast)
13. Al 5052-0
14. Al 5052-H12
15. Al 5456-0, H353
16. Al 5052-H32
17. Al 1100-0
18. Al 3003-H25
19. Al 6061-T6
20. Al A360 (die cast)
21. Al 7075-T6
22. Al 6061-0

23. Indium
24. Al 2014-0
25. Al 2024-T4
26. Al 5052-H16
27. Tin (plated)
28. Stainless steel 430 (active)
29. Lead
30. Steel 1010
31. Iron (cast)
32. Stainless steel 410 (active)
33. Copper (plated, cast, or wrought)
34. Nickel (plated)
35. Chromium (Plated)
36. Tantalum
37. AM350 (active)
38. Stainless steel 310 (active)
39. Stainless steel 301 (active)
40. Stainless steel 304 (active)
41. Stainless steel 430 (active)
42. Stainless steel 410 (active)
43. Stainless steel 17-7PH (active)
44. Tungsten
45. Niobium (columbium) 1% Zr
46. Brass, Yellow, 268
47. Uranium 8% Mo.
48. Brass, Naval, 464
49. Yellow Brass

50. Muntz Metal 280
51. Brass (plated)
52. Nickel-silver (18% Ni)
53. Stainless steel 316L (active)
54. Bronze 220
55. Copper 110
56. Red Brass
57. Stainless steel 347 (active)
58. Molybdenum, Commercial pure
59. Copper-nickel 715
60. Admiralty brass
61. Stainless steel 202 (active)
62. Bronze, Phosphor 534 (B-1)
63. Monel 400
64. Stainless steel 201 (active)
65. Carpenter 20 (active)
66. Stainless steel 321 (active)
67. Stainless steel 316 (active)
68. Stainless steel 309 (active)
69. Stainless steel 17-7PH (passive)
70. Silicone Bronze 655
71. Stainless steel 304 (passive)
72. Stainless steel 301 (passive)
73. Stainless steel 321 (passive)
74. Stainless steel 201 (passive)
75. Stainless steel 286 (passive)
76. Stainless steel 316L (passive)

77. AM355 (active)
78. Stainless steel 202 (passive)
79. Carpenter 20 (passive)
80. AM355 (passive)
81. A286 (passive)
82. Titanium 5A1, 2.5 Sn
83. Titanium 13V, 11Cr, 3Al (annealed)
84. Titanium 6Al, 4V (solution treated and aged)
85. Titanium 6Al, 4V (anneal)
86. Titanium 8Mn
87. Titanium 13V, 11Cr 3Al (solution heat treated and aged)
88. Titanium 75A
89. AM350 (passive)
90. Silver
91. Gold
92. Graphite

Noble (Less Active, Cathodic)

الخلاصة

للأهميةِ المتزايدةِ للتآكلِ في كُلّ فروعِ الحياةِ الأخيرةِ , دراسة على سلوكِ المعادنِ الاكثر الصناعيةِ (خارصين, حديد و نحاس) في حامضِ الهيدروليك مُقَدَّمُة في هذه الإطروحةِ.

إستعملتْ المعادنُ هنا حديد، نحاس وخارصين. أولاً تآكل هذه المعادنِ تُدْرَسُ نظرياً وتُقارنُ بالعملِ التجريبيِ، ثمّ نفس التحليلِ يُحتَفظُ بالدراسةِ المُقَدَّمةِ لتَوضيح التآكلِ الحر لكُلّ إزدواج كهربائي معدني ونظام الثلاثي الكهربائي هذه المعادنِ.

أجري التحليل للدالة الحامضية=0.7، ودرجات حرارة (30, 45 و60 °م) ولنِسَبِ مساحةِ (0.5, 1 و2) للمقارنةِ بالعملِ التجريبيِ. التحليل الآخر كَانتْ للمدى الاس الحامضي (1-3) ، مدى درجاتِ حرارة (20-60°م) وكسور منطقةِ الخارصينِ (0.1 لنظامِ واحد، 0.5 لنظامِ إثنان، 0.1 لنظامِ ثلاثة، 0.8 لنظامِ أربعة، 0.1 لنظامِ خمسة، 0.1 لنظامِ ستّة 0.4 لنظامِ سبعة)، مِنْ النحاسِ (0.1 لنظامِ واحد، 0.1 لنظامِ إثنان، 0.5 لنظامِ ثلاثة، 0.1 لنظامِ أربعة، 0.8 لنظامِ خمسة، 0.4 لنظامِ ستّة 0.5 لنظامِ سبعة) ومِنْ الحديدِ (0.8 لنظامِ واحد، 0.4 لنظامِ إثنان، 0.4 لنظامِ ثلاثة، 0.1 لنظامِ أربعة، 0.1 لنظامِ خمسة، 0.5 لنظامِ ستّة 0.1 لنظامِ سبعة).

استنتج في الدراسة أنّ النَتائِجَ المَحْسُوبة قُرْب النَتائِجِ التجريبيةِ، والإزدواج الكهربائي متزايدةُ نسبةُ تآكلَ المعدنِ الموجب القطبِ تحت شرطِ التآكلِ الحرِ، ونظام الثلاثي الثلاثيُ نسبة تآكلِ.

في كُلّ الشروطِ، الإختلاف في شروطِ النظامَ كالتّالي: زيادة في درجةِ الحرارة تَزِيدُ تيارَ التآكلَ لكن تَنْقصُ إمكانية التآكلَ في القيمةِ الثابتةِ للاس الحامضي. زيادة في الاس الحامضي تَزِيدُ إمكانية التآكلَ في حين تَنْقصُ تيارَ التآكلَ عندما تُثبّتُ درجة حرارة.

شكر وتقدير

في البداية أشكر الله عز وجل الذي وفقني لاكمال متطلبات هذا البحث. وبعد الانتهاء من بحثي لا يسعني الا ان أقدم شكري واحترامي وتقديري للدكتور باسم عبيد حسن لاقتراحه موضوع الرسالة ولاشرافه على بحثي ومتابعته الدائمة ولاراءه السديدة واقتراحاته وتوجيهاته القيمة طيلة فترة البحث.

كما أود تقديم جزيل شكري رئيس قسم الهندسة الكيمياوية الاستاذ الدكتور قاسم جبار سليمان لمساندته القيمة طيلة فترة البحث.

ولا يسعني الا أن أشكر جميع أساتذة قسم الهندسة الكيمياوية لمساعدتهم القيمة اثناء بحثي.

وان اشكر الاستاذ الدكتور عميد كلية الهندسة لتذليله العقبات التي واجهتني اثناء دراستي؛ كما اشكر جميع العاملين في العمادة للاسناد المتواصل خلال الدراسة.

و أود أن اشكر وأقدم امتناني جميع افراد عائلتي لتفهمهم ومساعدتهم وتيسيرهم العقبات طوال فترة دراستي والى نبع الحنان ابي وامي.

ولا انسى ان أشكر شقيق والدي المدرس المساعد عبد الله خضير عباس لدعمه و توفيره لبعض المصادر الخاصة بالبحث.

م. أسيل فاضل خضير

التحليل النظري للتأكل المعدني الغلفاني (الخارصين ، الحديد والنحاس) تحت سيطرة طاقة التنشيط

رسالة
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وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية

من قبل

أسيل فاضل خضير عباس
(بكالوريوس علوم في الهندسة الكيمياوية 2004)

جمادى الأخر 1430
حزيران 2009