



**Chemical kinetics and Electrochemistry Examination for M. Sc. Students**

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**Section A**

**Answer the following questions: (40 marks)**

1- Answer the following questions:

a- What are the different types of polarization, explain in details the concentration polarization.

**OR** the effect of polarization and the resistance of the electrolyte on corrosion rate.

b- Explain the kinetic theory of corrosion. Sketch the polarization curve of corroding metal.

2- Define corrosion. Sketch and describe the Pourpaix Fe-H<sub>2</sub>O diagram taking in consideration the limitations should be considered using this diagram in prediction of metallic corrosion.

With my best wishes  
Prof. Dr. El-Sayed Mabrouk

## Model Answer

### Answer of question No. 1:

#### a-Types of polarization:

There are three types of polarization, resistance or ohmic polarization, activation polarization and concentration polarization.

Concentration polarization:

It is well known that in an electrolytic processes, the concentration of the electrochemically active materials in the immediate vicinity of the electrode is different from that in the bulk of solution, thus in cathodic deposition process, the concentration of metal ions around the cathode is smaller than that in the bulk of the solution and in anodic process the reverse is occurred. During the discharge of cations at the cathode, ions are brought to the electrode surface by three ways: i) ionic migration, ii) diffusion, iii) agitation (stirring or convection). IF the total supply of ions by (i) and (ii) is adequate, there no ionic transport by diffusion, but if the rate of electrolysis exceed that at which ions can be brought by (i) and (iii), then the electrolyte concentration at the electrode surface falls below in the bulk of the solution and ionic transport by diffusion takes place. An equilibrium is then reached in which a concentration gradient exist in a thin layer of solution ( $d$ ) adjacent to the electrode. The position of this equilibrium is controlled by the rate of diffusion. The activity of the diffusing particles in the bulk is  $a$  and that at the electrode surface is  $a_e$  and the rate of diffusion is proportional with the difference between these two activities and is given by the following relation:

$$\text{Rate of diffusion} = D/d (a - a_e)$$

in which  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{sec}$ . The value of  $D$  for most cations are near to the value  $7.5 \times 10^{-6} \text{ cm}^2/\text{sec}$  for  $\text{H}^+$  and  $\text{OH}^-$  ions they are several times greater than most ions. Besides transport of ions by diffusion, an electrolytic transport according to Faraday's law occurs according to the following equation: Rate of

$$\text{electrolytic transport} = n_+ i / ZF$$

In which  $n_+$  is transport number of cations,  $i$  is current density in ampere /  $\text{cm}^2$ ,  $F$  is the Faraday constant (96500 coulombs). The total rate of transport ( $i/ZF$ ) is given by the following relation:

$$i / ZF = D/d (a - a_e) + n_+ i / ZF$$

$$i / ZF - n_+ i / ZF = D/d (a - a_e)$$

$$(1 - n_+) i / ZF = D/d (a - a_e)$$

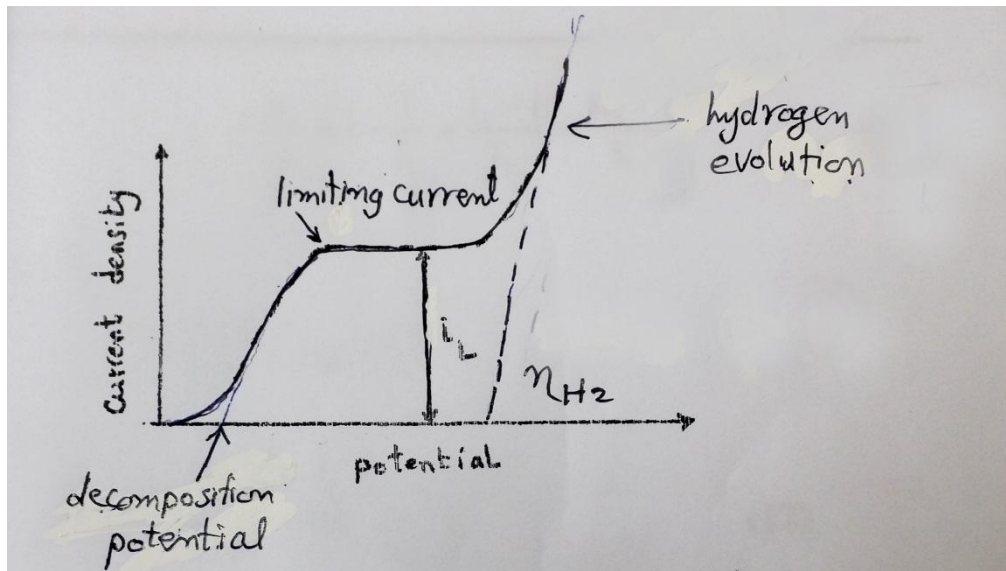
$$i = ZFD / (1 - n_+)d (a - a_e)$$

From the last equation, as the value of  $i$  is increased value of  $a_e$  decreases and zero value of  $a_e$  corresponds to the maximum value of  $i$ , which is known as limiting current,  $i_L$ . In this situation, the limiting current is given by the relation:

$$i_L = ZFD a / (1 - n_+) d = ZFD a / n d$$

where  $n$  represents the sum of transport number of all ions which are discharged at the cathode. The last equation can be written as:  $i_L = k a$  (where  $k$  is a constant)

Practically under the limiting current conditions the electrode potential increases until some different electrode reaction with a great limiting current is able to proceed such as hydrogen evolution. The general form of the relation between concentration polarization (overpotential) and current is shown in the following figure:



The section of the curve up to the limiting current in the figure is expressed by the following equation: i- At the electrode surface, the potential is given by:

$$e = e^{\circ} + RT / ZF \ln a_e$$

ii- The reversible electrode potential is given by:

$$e_{rev} = e^{\circ} + RT / ZF \ln a$$

The concentration overpotential is given by:

$$\eta_c = e - e_{rev} = RT / ZF \ln a_e / a$$

By dividing equation 5 over equation 8 we get:

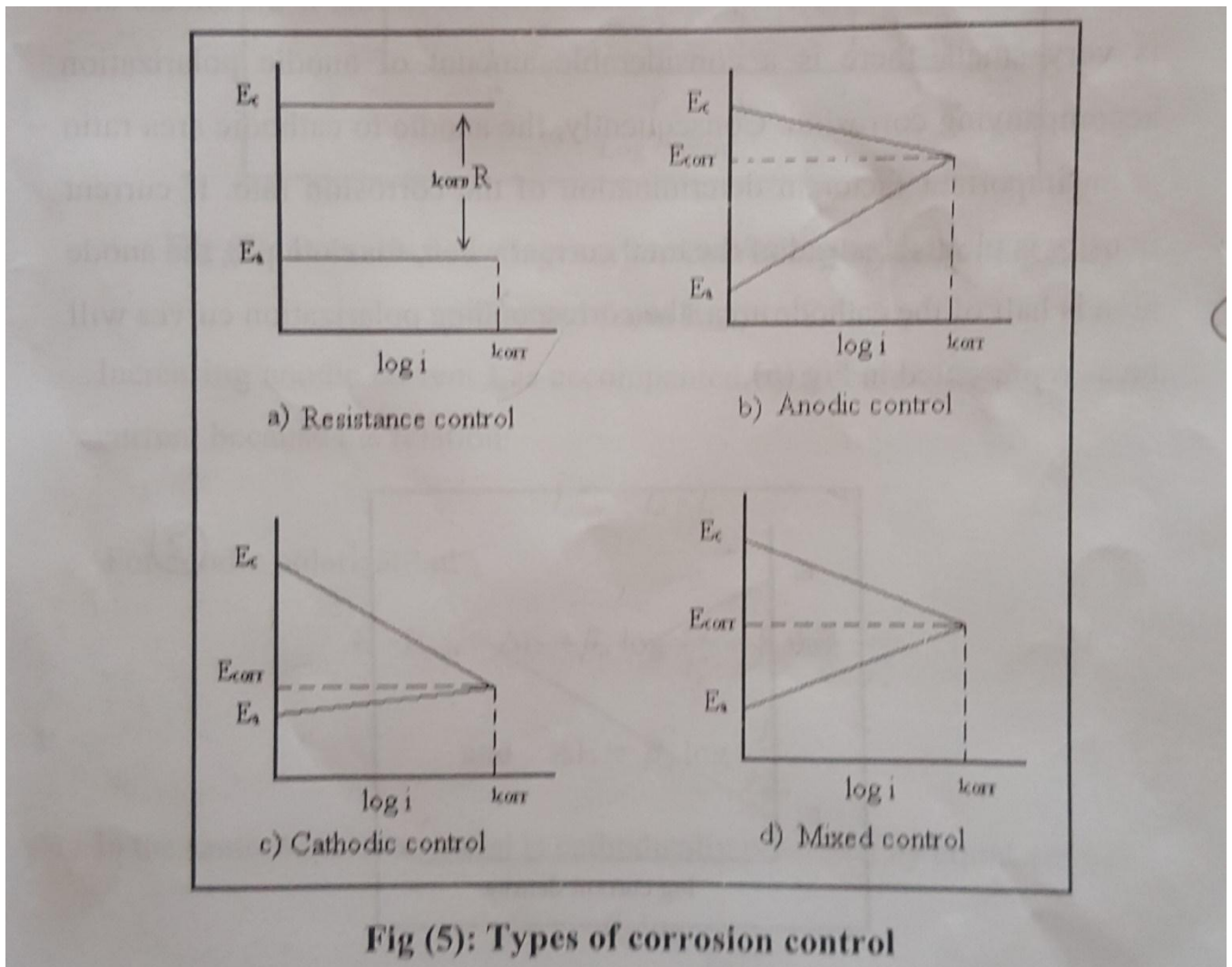
$$a_e / a = i_L - i / i_L, \text{ therefore } \eta_c = 2.303 RT / ZF \log i_L - i / i_L$$

**. a- Effect of polarization on corrosion rate:**

There are many factors which affect the corrosion reaction mainly by changing the polarization characteristics of one or more of the electrode reactions. Firstly, the resistance of the

electrolyte is one of these factors. When the resistance of the electrolyte is high, the resultant current is not sufficient to cause polarization neither for anodic or cathodic reactions. In this case the corrosion process is said to be under resistance control as shown in Fig. (a). This mechanism is applied for example in case of a porous insulator cover the metal surface and the corrosion current is then controlled by IR drop in the pores of coating.

Secondly, when polarization occurs mainly on the anodic area (Fig. b), the corrosion reaction is thus anodically control. The corrosion potential is closed to the equilibrium potential of the cathode. On the other hand, if the polarization is mostly cathodic, the corrosion is considered to be cathodically control and the corrosion potential is closed to the equilibrium potential of the anode (Fig. c). If the polarization occurs with the same degree at both anode and cathode, the corrosion reaction is said to be mixed control (Fig. d).



**Fig (5): Types of corrosion control**

Thirdly, the polarization depends besides the nature of electrode and electrolyte on the actual area of the electrode. If the anodic area is very small, there is a considerable amount of anodic polarization accompany corrosion. Thus, the anodic to cathodic area ratio is an important factor in determining the cor

**b- Kinetic theory of corrosion:**

Thermodynamics deals with the corrosion reaction energy and its equilibrium potential. Thermodynamics failed in expression of the corrosion rate and interpretation of corrosion of ultra pure metals. Thus, these two point are well covered by the kinetic theory of corrosion. This theory consists of two simple hypotheses:

- 1- Every electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
- 2- No accumulation of the electrical charge can occur during an electrochemical reaction.

To illustrate the application of the kinetic theory of corrosion, consider the following figure which represents the polarization diagram of corroding metal (M) in acidic aqueous solution. The cathodic reaction will be the discharge of hydrogen which takes place also at the surface of corroding metal. When metal is not corroded, it is in reversible equilibrium with the solution and have equilibrium potential  $E_{M^+/M}$  with exchange current density  $i_{o, M^+/M}$ . On the other hand, if this non-corroded metal is saturated with hydrogen gas at unit activity and pressure, it behaves as hydrogen electrode and will assume the equilibrium electrode potential  $E_{H^+/H}$  with exchange current density  $i_{o, H^+/H}$ .

During a uniform corrosion process, the two individual electrode potential for metal and hydrogen gas are polarized toward each other until both acquire a value of the corrosion potential (mixed potential). The value of the current corresponds to the corrosion potential is the corrosion current density (the rate of corrosion). It could be recognized in the figure that the mixed potential have a value between the two equilibrium potentials of oxidation and reduction reactions. The polarization diagram in the figure is an example illustrates the way of representing the kinetic data of corrosion graphically which is also called Evan diagram, where the anodic and cathodic areas are the same.

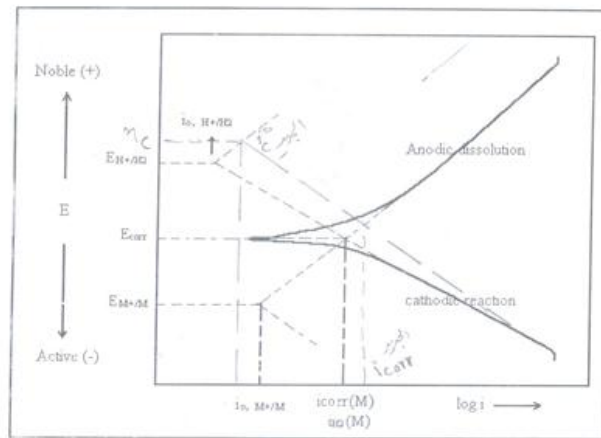
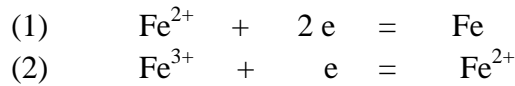


Fig ( 1): Polarization curves for corroding metal (M)

**Answer of question No. 2:**

Pourbaix diagram of for corrosion behavior of iron – water system is represented in the following figure. The diagram contains three types of straight lines, horizontal, vertical and sloping lines. The horizontal lines which parallel to the pH axis represents equilibrium does not depend on the pH value. Thus, lines (1) and (2) represent the following equilibrium reactions, respectively:



Both reactions do not involve  $\text{H}^+$  ions while involve electrons and thus, they have been shown as horizontal lines in Pourbaix diagram. On the other hand, the vertical lines which is parallel to the potential axis represents an equilibrium does not depend on potential value. Thus, electrons do not involve while protons are present in the equilibrium reaction as represented in reaction 3:



The equilibrium reaction which depend on both the potential and the pH value is represented by the sloping line (4):  $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$

It should be noted that the equilibrium reaction involves both protons and electrons. As have be described, Pourbaix diagram gives collected information about different products resulted from the reaction of the metal with the environment, at different pH and potential values. This enables us to predict the corrosion behavior of metal in aqueous medium at a given potential and pH values. The diagram also involves three areas, the area which represented the pure metal indicate that the metal does not react at all with the environment and called immunity area. On the other hand, the area which represents a formation of soluble compound is a corrosion area. The third area is that represents the formation of insoluble compound which acts as a barrier between the metal and the environment and preventing the metal corrosion. This area is called the passive area.

The limitation of the Pourbaix diagram is that , it does not give any information about the rate of corrosion, also the term passivity is used by it for describing the formation of sparingly soluble compounds, however these compounds may be formed but not on the electrode surfsce, and thus they do not give rise to passivation of the metal. Also, the diagram does not take in account the presence of extraneous ions in the medium or impurities in the metal.

