



**Chemistry Department**  
**Faculty of Science**  
**Benha University**

**Advanced**  
**Physical Chemistry**  
**(Chem 447)**

**2 /1/2019**

**Time: 2 hr**

---

---

**I- Choose the right answer for twenty only of the following: (40 marks)**

- 1- Galvanic cell is defined as:
  - a- A cell which converted the electrical energy to chemical energy.
  - b- A cell which converted the chemical energy to electrical energy.
  - c- A cell which converted the electrical energy to heat energy.
  
- 2- If the metal has a curved surface:
  - a- The more highly convex surface is the anodic area.
  - b- The less highly convex surface is the anodic area.
  - c- The more highly convex surface is the cathodic area.
  
- 3- In concentration cells:
  - a) The electrode which in contact with the dilute solution is the cathode.
  - b) The electrode which in contact with the concentrated solution is the anode.
  - c) The electrode which in contact with the dilute solution is the anode.
  
- 4- In the electrochemical cell have different aeration:
  - a) The electrode which exposed to higher oxygen is the anode.
  - b) The electrode which exposed to lower oxygen is the anode.
  - c) The electrode which exposed to lower oxygen is the cathode.
  
- 5- The dissolution of metals will occur if:
  - a)  $\Delta G$  has + ve value.
  - b)  $\Delta G$  has – ve value.
  - C)  $\Delta G$  equals to zero.
  
- 6- In the electromotive series the tendency of metal ions to electro deposition:
  - a) Increases as going from the top to the bottom of the series.
  - b) Decreases as going from the top to the bottom of the series.
  - c) Increases as going from the bottom to the top of the series.
  
- 7- In the electrochemical series:
  - a) The metal which has a more negative  $E^{\circ}$  will corrode.
  - b) The metal which has a less negative  $E^{\circ}$  will corrode.
  - c) The metal which has a more negative  $E^{\circ}$  will deposit.
  
- 8- In the thermodynamic stability diagram of water the area above the line of equilibrium potential of oxygen represents:
  - a) The decomposition of  $H_2O$  and  $OH^-$  is obtained.

- b) The decomposition of  $\text{H}_2\text{O}$  and  $\text{H}^+$  is obtained.  
 c) The formation of  $\text{H}_2\text{O}$  from the combination of  $\text{O}_2$  gas and  $\text{H}^+$  ions.
- 9- In standard hydrogen electrode, the standard potential  $E^\circ$  depends on:  
 a- The concentration of  $\text{H}^+$  ion in the solution.  
 b- The pressure of the hydrogen gas.  
 c- Both the  $\text{H}^+$  ion concentration and pressure of hydrogen gas.
- 10- In galvanic series:  
 a) Metals in the top are noble while those in the bottom are active.  
 b) The effects of temperature and pH on the corrosion were taken in contact.  
 c) The corrosion of metals depends not only on their positions in the electromotive series but also on the polarization in the different environments.
- 11- The rate-determining step of an electro-chemical re  
 a- Is the faster step.                      b- Is the slowest step.                      c- Is the moderate step.
- 12- The mathematical expression of Nernst equation is:  
 a-  $\Delta G^\circ = -ZFE^\circ$                       b-  $E = E^\circ + \frac{RT}{ZF} \ln (a_O / a_R)$   
 c-  $\Delta G = \Delta G^\circ + RT \ln (a_P / a_R)$
- 13- The exchange current density ( $i_o$ ) can be defined as:  
 a) The rate of oxidation reaction when an oxidation current is passed.  
 b) The rate of reduction reaction when a reduction current is passed  
 c) The rate of oxidation or reduction of the electrode reaction at its equilibrium state.
- 14- Activation polarization occurs due to:  
 a) The concentration gradient between the bulk and the electrode surface  
 b) The resistance of the electrolyte solution in the electrochemical cell  
 c) A slow electrode reaction occurs such as hydrogen evolution.
- 15- Resistance polarization decreases:  
 a) As the distance between the two electrodes increases  
 b) As the distance between the two electrodes decreases.  
 c) Not affected by the distance between the two electrodes.
- 16- For normal hydrogen electrode:  
 a)  $E_{\text{H}_2} = -0.0591 \text{ pH}$                       b)  $E_{\text{H}_2} = 0.0591 \text{ pH}$                       c)  $E_{\text{H}_2} = \text{zero}$
- 17- In a cell consists of two identical electrodes immersed in the same electrolyte:  
 a) The electrode which exposed to the lower oxygen will be the cathode.  
 b) The electrode which exposed to the lower oxygen will be the anode.  
 c) The electrode which exposed to the higher oxygen will be the anode.

- 18- In Daniel cell, the cathodic reaction is:
- a) The deposition of copper ions.
  - b) The deposition of zinc ions.
  - c) The dissolution of zinc metal.
- 19- In galvanic cell consists of iron electrode ( $E^{\circ} = - 0.44\text{V}$ ) and zinc electrode ( $E^{\circ} = - 0.76\text{V}$ ):
- a) Zinc metal is dissolved.
  - b) Iron metal is dissolved.
  - c) Zinc ions are deposited.
- 20- In standard hydrogen electrode, the standard potential  $E^{\circ}$  depends on:
- a) The concentration of hydrogen ions in the electrolyte.
  - b) The pressure of the hydrogen gas.
  - c) Both (a) and (b).
- 21- In concentration cells composed of two identical electrodes immersed in the same electrolyte:
- a) The electrode which in contact with the dilute solution is the cathode.
  - b) The electrode which in contact with the concentrated solution is the anode.
  - c) The electrode which in contact with the dilute solution is the anode.
- 22- If the surface of the metal has different strain:
- a) The strained area is usually the cathodic area.
  - b) The strained area is usually the anodic area.
  - c) The unstrained area is usually the anodic area.
- 23- If the metal surface is exposed to differential illumination:
- a) The darker region of the surface will be the cathode.
  - b) The brighter region of the surface will be the anode.
  - c) The darker region of the surface will be the anode.
- 24- According to the electromotive series, corrosion of metals in de-aerated aqueous solution is:
- a) The reduction of oxygen gas in the electrolyte solution.
  - b) The reduction of hydrogen ions and hydrogen gas is evolved.
  - c) The oxidation of hydroxide ions and oxygen gas is evolved.
- 25- The local action cell theory postulate that:
- a) The corrosion tendency of the metal increases as the amount of the impurities contained in the metal decreases.
  - b) The corrosion tendency of the metal increases as the amount of the impurities contained in the metal increases.
  - c) The amount of the impurities contained in the metal not affected on the tendency of corrosion

## II- Answer the following questions:

- 1- Sketch and describe in details the Pourbaix diagram of Fe-H<sub>2</sub>O system. (15 marks)
- 2- Write in details on the kinetic theory of corrosion and the polarization curve of corroding metal. (15 marks)
- 3- Answer one only (a) or (b) of the following: (10 marks)
  - a) Sketch and describe in details the calomel electrode.
  - b) Sketch and describe graphically the effect of resistance and polarization on the corrosion potential.

## Model Answer

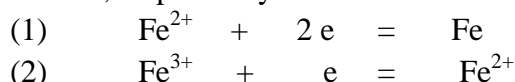
### Answer of question No. I:

- 1- b) A cell which converted the chemical energy to electrical energy.
- 2- a) The more highly convex surface is the anodic area.
- 3- c) The electrode which in contact with the dilute solution is the anode.
- 4- b) The electrode which exposed to lower oxygen is the anode.
- 5- b)  $\Delta G$  has -ve value.
- 6- a) Increases as going from the top to the bottom of the series.
- 7- a) The metal which has a more negative  $E^0$  will corrode.
- 8- b) The decomposition of H<sub>2</sub>O and H<sup>+</sup> is obtained.
- 9- c) Both the H<sup>+</sup> ion concentration and pressure of hydrogen gas.
- 10- c) The corrosion of metals depends not only on their positions in the electromotive series but also on the polarization in the different environments.
- 11- b) Is the slowest step.
- 12- b)  $E = E^0 + \frac{RT}{ZF} \ln (a_O / a_R)$ .
- 13- c) The rate of oxidation or reduction of the electrode reaction at equilibrium state.
- 14- c) A slow electrode reaction occurs such as hydrogen evolution.
- 15- b) As the distance between the two electrodes decreases.
- 16- a)  $E_{H_2} = - 0.0591 \text{ pH}$ .
- 17- c) The electrode which exposed to the higher oxygen will be the anode.
- 18- a) The deposition of copper ions.
- 19- a) Zinc metal is dissolved.
- 20- c) Both (a) and (b).
- 21- a) The electrode which in contact with the dilute solution is the cathode.
- 22- b) The strained area is usually the anodic area.
- 23- c) The darker region of the surface will be the anode.
- 24- b) The reduction of hydrogen ions and hydrogen gas is evolved.
- 25- b) The reduction of hydrogen ions and hydrogen gas is evolved.

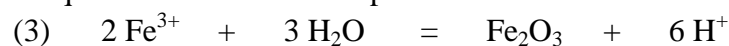
## Answer of question No. II 1:

1-Pourbaix diagram of Fe-H<sub>2</sub>O system:

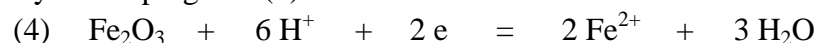
Pourbaix diagram of for corrosion behavior of iron – water system is represented in the following figure. The diagram contains three types of straight lines, horizontal, vertical and sloping lines. The horizontal lines which parallel to the pH axis represents equilibrium does not depend on the pH value.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



Both reactions do not involve H<sup>+</sup> 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:

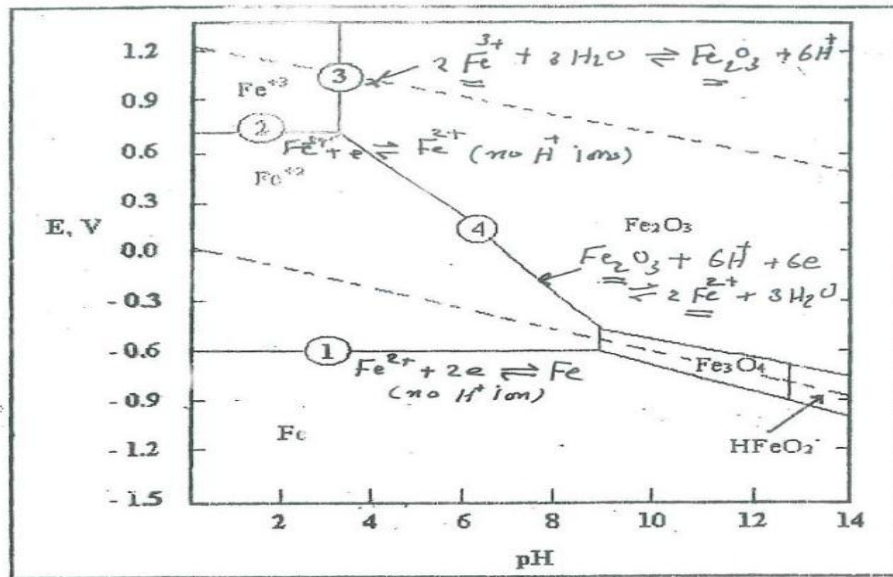


The equilibrium reaction which depend on both the potential and the pH value is represented by the sloping line (4):



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.



## Answer of question No. II 2:

Kinetic theory of corrosion:

Kinetic theory of corrosion postulate that:

- 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.

Both the anodic and cathodic reactions should proceed at the same time with equal rates. Thus, electrons provided by anodic reaction are consumed by the cathodic one. To illustrate the application of the kinetic theory of corrosion consider the following figure which represents the polarization diagram of corroding metal (M) in an acidic aqueous solution in which the cathodic reaction will be the discharge of hydrogen ions which take place also at the surface of corroding metal. When the metal is not corroded, it is in reversible equilibrium with the solution and has equilibrium potential  $E^{\circ}_{M^+/M}$  with exchange current  $i_{o, M^+/M}$ . On the other hand, if the non-corroded metal is saturated with hydrogen gas at unit activity and unit pressure, it behaves as a hydrogen electrode and will assume the equilibrium electrode potential of hydrogen,  $E^{\circ}_{H^+/H_2}$  with exchange current density  $i_{o, H^+/H_2}$ . From the figure it is clear that during the uniform corrosion process, the two individual electrode potentials ( $E^{\circ}_{M^+/M}$  &  $E^{\circ}_{H^+/H_2}$ ) are polarized toward each other until both acquire a value of corrosion potential  $E_{corr}$  (mixed potential). The value of current corresponding to the corrosion potential is the corrosion current  $i_{corr}$  density (rate of corrosion). As shown in the figure, the mixed potential ( $E_{corr}$ ) has a value between the two equilibrium potentials (potential of oxidation and potential of reduction). The explained polarization diagram representing the kinetic data of corrosion graphically. This type of representation is called also Evans diagram. The curves of the polarization

diagram are restricted to the uniform type of corrosion where the anodic and cathodic areas are the same.

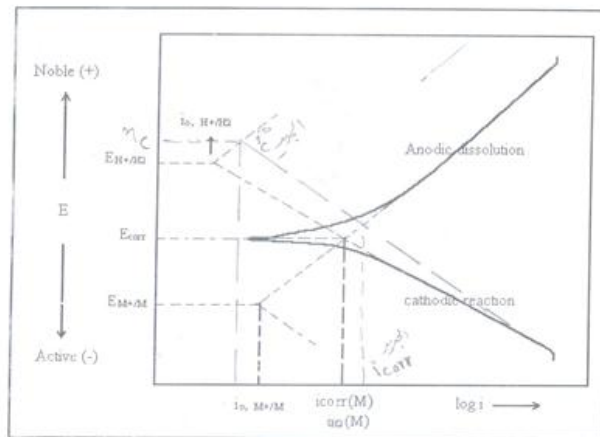
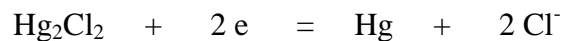


Fig ( 1 ): Polarization curves for corroding metal (M)

**Answer of question No. II 3:**

3a: calomel electrode:

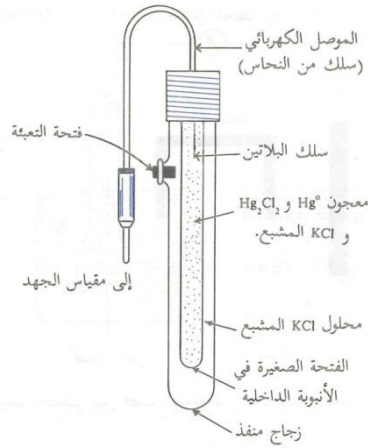
calomel electrode is the most frequently used reference electrode in the laboratory. It consists of a pool of mercury covered with a layer of mercurous chloride (calomel) and immersed in solution of potassium chloride acting as the electrolyte as shown in the following figure. The electric contact to mercury is made by a platinum wire. The overall reaction takes place in calomel electrode is:



Applying Nernst equation the potential of the electrode can be determined as follows:

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

This equation indicates that the potential of the calomel electrode depends on the activity of chloride ions. Three types of calomel electrode containing different chloride ion concentrations are commonly used which are 0.1 N, 1.0 N and saturated potassium chloride, the potentials of which are 0.335, 0.281 and 0.242, respectively. As the concentration of chloride ions is increased the potential of the above electrodes decreases. The temperature coefficient for the three electrodes are - 0.06, - 0.24 and - 0.65, respectively.



### 3b: 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).

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 corrosion rate. If the current density is plotted against potential, for example, when the anode area is half of the cathode one, the corresponding polarization curves as represented in the following curves will be obtained.



