



Examination of Applied Electrochemistry 1

Answer the following questions:

I- Choose the right answer in the following: (44 marks)

- 1) The Flade potential (E_F):
 - a) Increases toward noble direction as the acidity of the solution is increased.
 - b) Increases toward active direction as the acidity of the solution is increased.
 - c) Does not affect by acidity.
- 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 the electromotive series the tendency of metal to corrode:
 - 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.
- 4) 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 H_2O and H^+ is obtained.
 - c) The formation of H_2O from the combination of O_2 gas and H^+ ions.
- 5) In galvanic series:
 - a) Metals in the top are noble while those in the bottom are active.
 - b) The effect of pH on the corrosion was taken in consideration.
 - c) The corrosion of metals depends not only on their positions in the electromotive series but also on their polarization behavior in the different environment.
- 6) The corrosion tendency of the metals decreases as
 - a) The amount of impurities in the metal decreases.
 - b) The amount of impurities in the metal increases.
 - c) The amount of impurities in the metal has no effect on corrosion process.
- 7) At equilibrium potential:
 - a) The current passes in the electrochemical cell is an anodic current.
 - b) The current passes in the electrochemical cell is a cathodic current.
 - c) The current passes in the electrochemical cell equals zero.
- 8) The exchange current density (i_0) 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.

- 9) Activation polarization occurs due to:
- The concentration gradient between the bulk and the electrode surface.
 - The resistance of the electrolyte solution in the electrochemical cell.
 - A slow electrode reaction occurs such as hydrogen evolution.
- 10) Resistance polarization decreases:
- As the distance between the two electrodes increases.
 - As the distance between the two electrodes decreases.
 - Not affected by the distance between the two electrodes.
- 11) In a cell consists of two identical electrodes immersed in the same electrolyte:
- The electrode which exposed to the lower oxygen will be the cathode.
 - The electrode which exposed to the lower oxygen will be the anode.
 - The electrode which exposed to the higher oxygen will be the anode.
- 12) In Daniel cell, the cathodic reaction is:
- The deposition of copper ions.
 - The deposition of zinc ions.
 - The dissolution of zinc metal.
- 13) In galvanic cell consists of iron electrode ($E^{\circ} = - 0.44\text{V}$) and lead electrode ($E^{\circ} = - 0.13\text{V}$):
- Iron is dissolved.
 - Iron ions are deposited.
 - Lead ions are deposited.
- 14) In concentration cells composed of two identical electrodes immersed in the same electrolyte:
- The electrode which in contact with the dilute solution is the cathode.
 - The electrode which in contact with the concentrated solution is the anode.
 - The electrode which in contact with the dilute solution is the anode.
- 15) If the surface of the metal has different strain:
- The strained area is usually the cathodic area.
 - The strained area is usually the anodic area.
 - The unstrained area is usually the anodic area.
- 16) If the metal surface is exposed to differential illumination:
- The darker region of the surface will be the cathode.
 - The brighter region of the surface will be the anode.
 - The darker region of the surface will be the anode.
- 17) According to the electromotive series, the cathodic reaction in corrosion of metals in aerated aqueous solution is:
- The reduction of oxygen gas and hydroxyl ions are obtained.
 - The reduction of hydrogen ions and hydrogen gas is evolved.
 - The oxidation of hydroxide ions and oxygen gas is evolved.

- 18) In corrosion of metals:
- The corrosion rates in soil are higher than those in atmosphere.
 - The corrosion rates in soil are lower than those in atmosphere.
 - The corrosion rates in soil and atmosphere are the same.
- 19) In soil corrosion:
- As the depth at which the metal is buried increases the corrosion rate is decreased.
 - As the depth at which the metal is buried increases the corrosion rate is increased.
 - The depth at which the metal is buried has no effect on the rate of corrosion.
- 20) In soil corrosion, the presence of dissolved salts such as NaCl or Na₂SO₄:
- Increases the rate of corrosion.
 - Decreases the rate of corrosion.
 - Has no effect on the rate of corrosion.
- 21) In aqueous aerated solutions, the position of the metal in the electromotive series relative to hydrogen:
- Has no effect on the corrosion process.
 - Has an effect on the corrosion process.
 - The cathodic reaction is the discharge of H⁺ ions and H₂ gas is evolved.
- 22) In atmospheric corrosion:
- Hydrogen disulfide (H₂S) is the most harmful effect on corrosion of metals.
 - Sulfur dioxide (SO₂) is the most harmful effect on corrosion of metals.
 - Carbon disulfide (CS₂) is the most harmful effect on corrosion of metals.

II- Answer three only of the following questions:

- Describe in details the Pourbaix diagram of Fe-H₂O system. (12 marks)
- Write on the kinetic theory of corrosion. Sketch and explain the polarization diagram of a corroded metal. (12 marks)
- Define passivity. Give an account on galvanostatic anodic polarization of passivated metal. (12 marks)
- What are the factors affecting passivity. Write briefly on the effect of alloying elements, presence of passivators (oxidizers) or cathodic overpotential on passivity. (12 marks)

Model Answer

Answer of question number 1:

- 1) The Flade potential (E_F):
 - a) Increases toward noble direction as the acidity of the solution is increased. (•)
 - b) Increases toward active direction as the acidity of the solution is increased.
 - c) Does not affect by acidity.
- 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 the electromotive series the tendency of metal to corrode:
 - 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.
- 4) 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 H_2O and H^+ is obtained.
 - c) The formation of H_2O from the combination of O_2 gas and H^+ ions.
- 5) In galvanic series:
 - a) Metals in the top are noble while those in the bottom are active.
 - b) The effect of pH on the corrosion was taken in consideration.
 - c) The corrosion of metals depends not only on their positions in the series but also on their polarization behavior in the different environment. (•)
- 6) The corrosion tendency of the metals decreases as:
 - a) The amount of impurities in the metal decreases. (•)
 - b) The amount of impurities in the metal increases
 - c) The amount of impurities in the metal has no effect on corrosion.
- 7) At equilibrium potential:
 - a) The current passes in the electrochemical cell is an anodic current.
 - b) The current passes in the electrochemical cell is a cathodic current.
 - c) The current passes in the electrochemical cell equals zero. (•)

- 8) The exchange current density (i_0) can be defined as:
- The rate of oxidation reaction when an oxidation current is passed.
 - The rate of reduction reaction when a reduction current is passed
 - The rate of oxidation or reduction of the electrode reaction at its equilibrium state. (•)
- 9) Activation polarization occurs due to:
- The concentration gradient between the bulk and the electrode surface
 - The resistance of the electrolyte solution in the electrochemical cell
 - A slow electrode reaction occurs such as hydrogen evolution. (•)
- 10) Resistance polarization decreases:
- As the distance between the two electrodes increases
 - As the distance between the two electrodes decreases. (•)
 - Not affected by the distance between the two electrodes.
- 11) In a cell consists of two identical electrodes immersed in the same electrolyte:
- The electrode which exposed to the lower oxygen will be the cathode.
 - The electrode which exposed to the lower oxygen will be the anode. (•)
 - The electrode which exposed to the higher oxygen will be the anode.
- 12) In Daniel cell, the cathodic reaction is:
- The deposition of copper ions, (•)
 - The deposition of zinc ions.
 - The dissolution of zinc metal.
- 13) In galvanic cell consists of iron electrode ($E^\circ = -0.44V$) and lead electrode ($E^\circ = -0.13V$):
- Zinc is dissolved. (•)
 - Iron is dissolved.
 - Zinc ions are deposited.
- 14) In concentration cells composed of two identical electrodes immersed in the same electrolyte:
- The electrode which in contact with the dilute solution is the cathode.
 - The electrode which in contact with the concentrated solution is the anode.
 - The electrode which in contact with the dilute solution is the anode. (•)
- 15) If the surface of the metal has different strain:
- The strained area is usually the cathodic area.
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 - The unstrained area is usually the anodic area.
- 16) 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. (•)
- 17) According to the electromotive series, the cathodic reaction in corrosion of metals in 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.
- 18) In corrosion of metals:
- a) The corrosion rates in soil are little higher than those in atmosphere. (•)
 b) The corrosion rates in soil are little lower than those in atmosphere.
 c) The corrosion rates in soil and atmosphere are the same.
- 19) In soil corrosion:
- a) As the depth at which the metal is buried increases the corrosion rate is decreased.
 b) As the depth at which the metal is buried increases the corrosion rate is increased. (•)
 c) The depth at which the metal is buried has no effect on the rate of corrosion.
- 20) In soil corrosion, the presence of dissolved salts such as NaCl or Na₂SO₄:
- a) Increases the rate of corrosion. (•) b) Decreases the rate of corrosion.
 c) Has no effect on the rate of corrosion.
- 21) In aqueous aerated solutions, the position of the metal in the electromotive series relative to hydrogen:
- a) Has no effect on the corrosion process. (•)
 b) Has an effect on the corrosion process.
 b) The cathodic reaction is the discharge of H⁺ ions and H₂ gas is evolved.
- 22) In atmospheric corrosion:
- a) Hydrogen disulfide (H₂S) is the most harmful effect on corrosion of metals.
 b) Sulfur dioxide (SO₂) is the most harmful effect on corrosion of metals. (•)
 c) Carbon disulfide (CS₂) is the most harmful effect on corrosion of metals.

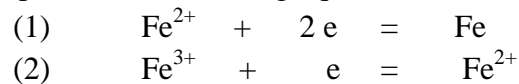
Answer of question No. II 1:

Pourbaix diagram of for corrosion behavior of iron – water system is represented in the following figure:

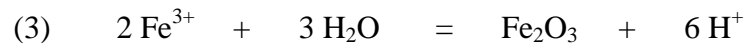
diagram contains three types of straight lines, horizontal, vertical and sloping lines. The horizontal

lines which parallel to the pH axis represents equilibrium does not depend on the pH value. Thus,

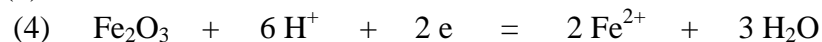
lines (1) and (2) represent the following equilibrium reactions, respectively:



Both reactions do not involve H^+ 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:

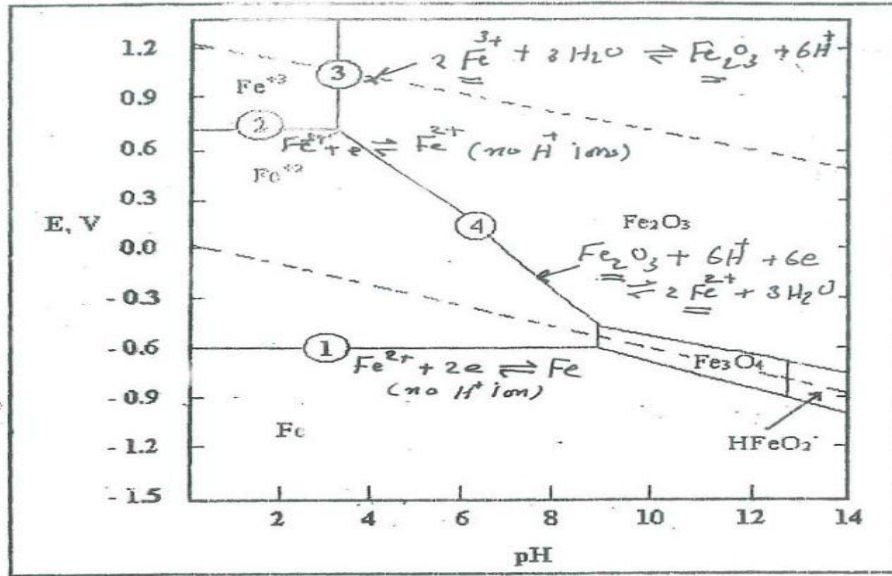


The equilibrium reaction which depend on both the potential and the pH value is represented by the sloping line (4) and reaction 4:



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 $E^0_{M^+/M}$ with exchange current $i_{0, M^+/M}$. 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, $E^0_{H^+/H_2}$ with exchange current density $i_{0, H^+/H_2}$. From the figure it is clear that during the uniform corrosion process, the two individual electrode potentials ($E^0_{M^+/M}$ & $E^0_{H^+/H_2}$) are polarized toward each other until both acquire a value of corrosion potential E_{corr} (mixed potential). The value of current corresponds 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.

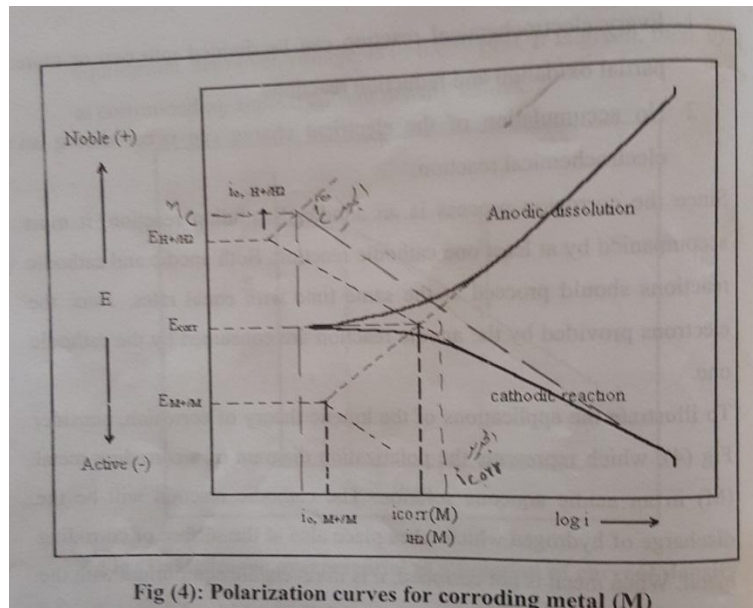
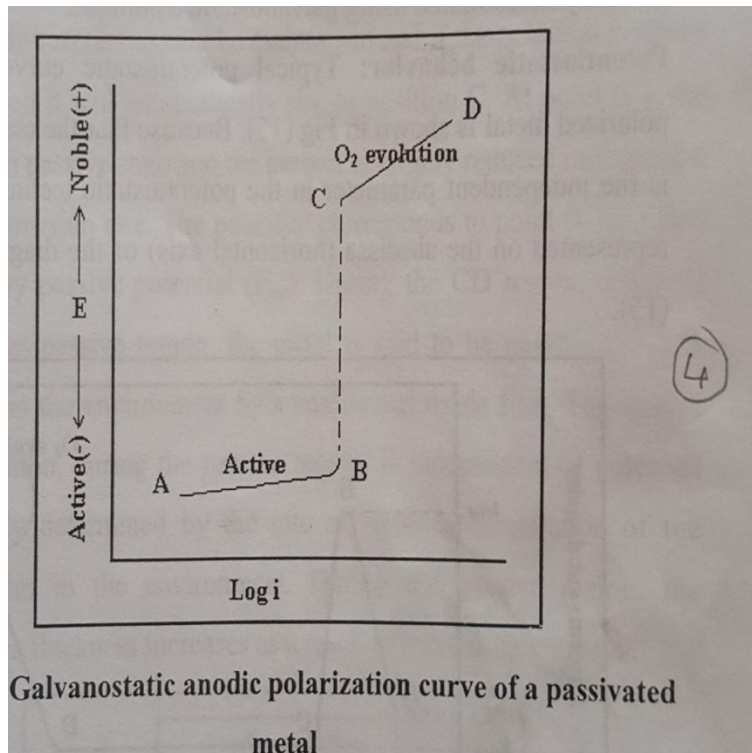


Fig (4): Polarization curves for corroding metal (M)

Answer of question No. II 3:

Passivity: Passivity is a phenomenon which observed during the electrochemical corrosion behavior of some metals. It is related with a decrease in corrosion rates of these metals upon increasing their potentials toward the noble direction. For example, it was found that iron reacts rapidly in dilute nitric acid but is visibly un-attacked by the concentrated acid. Upon removing iron from the concentrated acid and immersing it in the diluted one, there is a temporary state of corrosion resistance. This state of temporary corrosion resistance is called passivity. Thus, passivity can defined as a metal is passive if it substantially resists corrosion in a given environment resulting from marked anodic polarization. The electrochemical behavior of a passive metal can be studied using two different techniques. In both techniques the metal is anodically polarized in an electrochemical cell. in the first technique a current is applied to the metal and the change of metal potential according to the applied current value are recorded. This technique is known as galvanostatic polarization. The following diagram describes graphically the galvanostatic polarization curve of passivated metal.

The point A in the figure corresponding to the equilibrium potential between the metal and its ions and the corresponding current is the exchange current measured at equilibrium potential. Upon increasing the applied anodic current, the electrode potential polarized steeply toward the noble direction until the point B. Thus, the line AB represents the anodic dissolution reaction of the metal. If the applied anodic potential is increased beyond this point, the electrode potential increases suddenly to a value corresponds to point C. this behavior indicates that the electrochemical reaction is changed , i e, the metal dissolution is stopped and other anodic reaction. Probably, oxygen evolution is started. Thus, the line CD corresponds to the oxygen evolution reaction. The current density corresponds to point B is known as the critical current density. During the period BC, the metal is passive and is covered by a passive film.



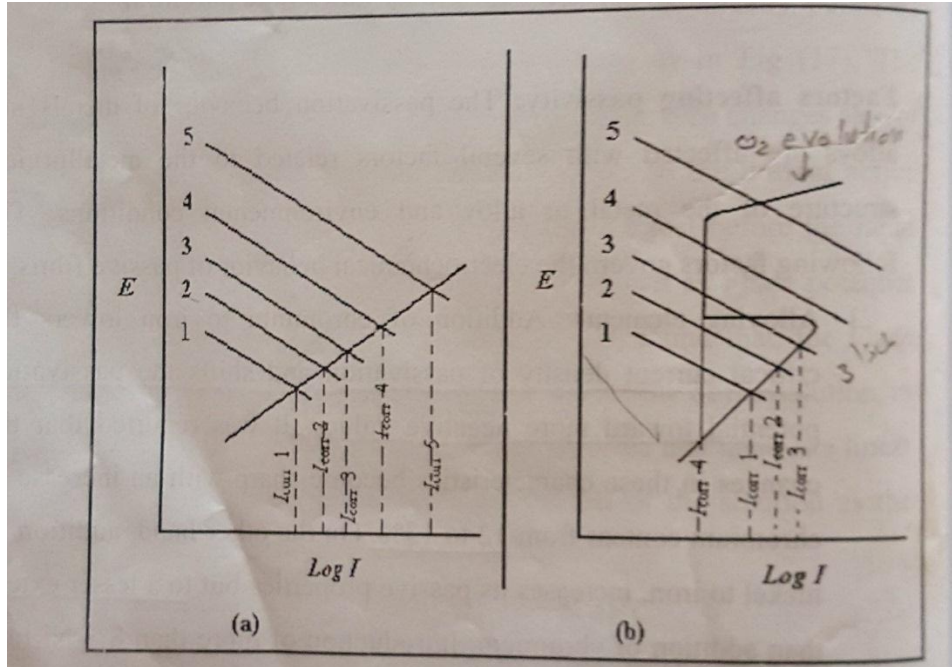
Answer of question No. II 4:

Factors affecting passivity:

The passivation behavior of metals and alloys are affected by several factors related to the metallurgical structure of the metal or alloy and environmental condition. These factors are, alloying elements, presence of passivators (oxidizer), cathodic overpotential, presence of halogen ions, temperature and pH.

- 1- Alloying elements: Addition of chromium to iron lowers the critical current density of passivation and shifts the potential toward more negative value. Also addition of nickel to iron increases its passive properties but to lesser extent than addition of chromium. Introduction of more than 8% nickel into chromium steel decreases the passivation current but shifts the passivation potential to more positive values. In general addition of more passive metal to a less passive metal normally lowers Flade potential and increases the ease of passivation.
- 2- Presence of passivators (oxidizers): Passivators are inorganic compounds behave as oxidizing agents which react only slowly with the metal when in direct contact but they are reduced more rapidly by cathodic currents. Therefore, they can adsorb on the metal surface adding cathodic area on it. As the concentration of passivator increases, the area occupied by its adsorbed anions increases and thus, the residual anodic area decreases. This situation obviously favors increased anodic polarization and ultimately passivation. Many inorganic compounds are known to be passivators such as chromates, nitrates, molybdates, tungstate and ferric ions. The effect of addition of oxidizer on the corrosion rate of normal and readily passivated metals is shown in the following figure. Addition of increasing concentrations of oxidizer shifts the reversible electrode potential to more positive values. As potential the

increases from 1 to 5 with increasing concentration, the corrosion rate increases from $I_{\text{corr } 1}$ to $I_{\text{corr } 5}$. However, the concentration rate increases as the oxidizer increases from 1 to 3. Increasing the concentration from 3 to 4 decreases the corrosion rate, since the metal attains passivity. On further increasing of concentration to 5, the corrosion rate increases again due to the metal corrosion in the trans-passive region.



3- Cathodic overpotential:

The decrease in cathodic overpotential caused by increase in case exchange current density and/or increase in Tafel slope, increases the corrosion rate of normal corroded metal. The effect is different in case of a metal exhibiting passivity. This effect is illustrated in the following figure which shows that as the overpotential decreases from 1 to 4 a decrease in concentration rate is observed due to attainment of passivity. The same effect is also obtained when a metal exhibiting passivity is alloyed with small amount of more noble metals having low hydrogen overpotential, such as Pd, Pt, or Cu or having low cathodic for the established cathodic reduction. This explains the behavior of stainless steel, which loss its passivity in dilute sulfuric acid and retains it when alloyed with Pd, Pt or Cu.

