



Model Answer

Question 1

A) *choose*

- 1- C 2- I 3- a 4- d 5- a

B) Consider the following reaction



Rate of forward reaction (Vf) = $K a_M e^{\alpha nF E / RT}$ 1

Rate of backward reaction (Vb) = $K^{-} a_{Mn+} e^{-(1-\alpha)nF E / RT}$ 2

At equilibrium

Rate of forward reaction (Vf) = Rate of backward reaction (Vb)

$$K a_M e^{\alpha nF E / RT} = K^{-} a_{Mn+} e^{-(1-\alpha)nF E / RT}$$
3

$$E^{\alpha nF E / RT} / e^{-(1-\alpha)nF E / RT} = K^{-} a_{Mn} / K a_M$$
4

$$e^{nF E / RT} = K^{-} a_{Mn} / K a_M$$
5

$$nF E / RT = \ln K^{-} / K + \ln a_{Mn} / a_M$$
6

equation 6 $\times RT/nF$

$$E = RT/nF \ln K^{-} / K + RT/nF \ln a_{Mn} / a_M$$
7

$$E = E^0 + RT/nF \ln a_{Mn} / a_M$$

$$E = E^0 + 0.0591/n \log a_{Mn} / a_M$$
 8

For the reaction



$$E = E^0 + 0.0591/n \log [C]^c [D]^d / [A]^a [B]^b$$

B)

$$E = E^0 - 0.0591 \log [Cl^-]$$

$$E_{\text{cell}} = E_c - E_a$$

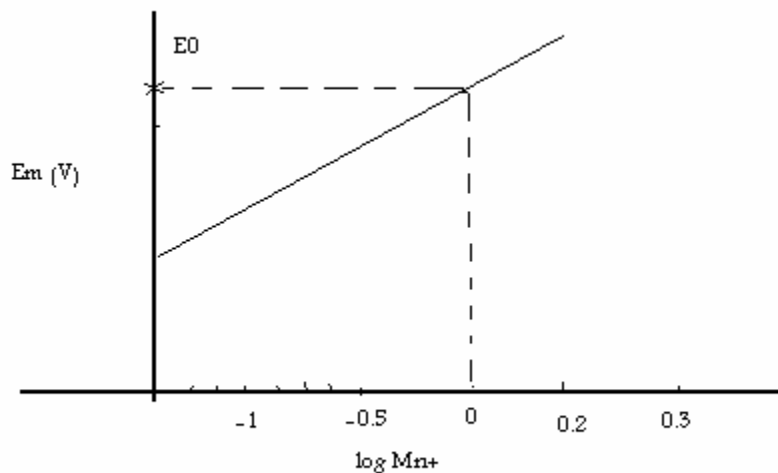
$$0.345 = 0.22 - E_a$$

$$E_a = 0.22 - 0.345$$

$$\log [Cl^-] = (0.22 - 0.345) / 0.0591$$

C) The potential of standard series of the ions are measured against suitable reference electrode. The measured potential is plotted against $\log [M^{n+}]$

The value of E_m at $\log [M^{n+}] = 0$ is E^0



Question 2

i-



anodic reaction

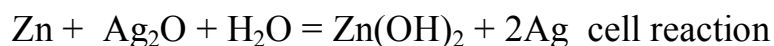
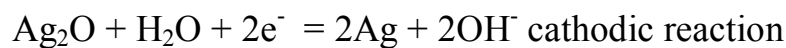
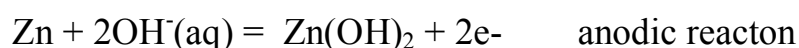


cathodic reaction



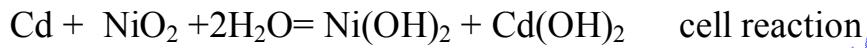
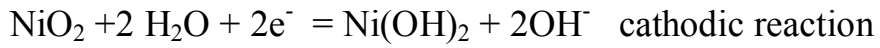
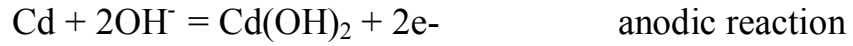
Cd 12.5%Hg / CdSO₄8/3 H₂O // CdSO₄(sat.aq) / Hg₂SO₄/Hg

ii-



Zn / OH⁻ // H₂O / Ag₂O the cell

iii-



Cd / OH⁻ // H₂O / NiO₂

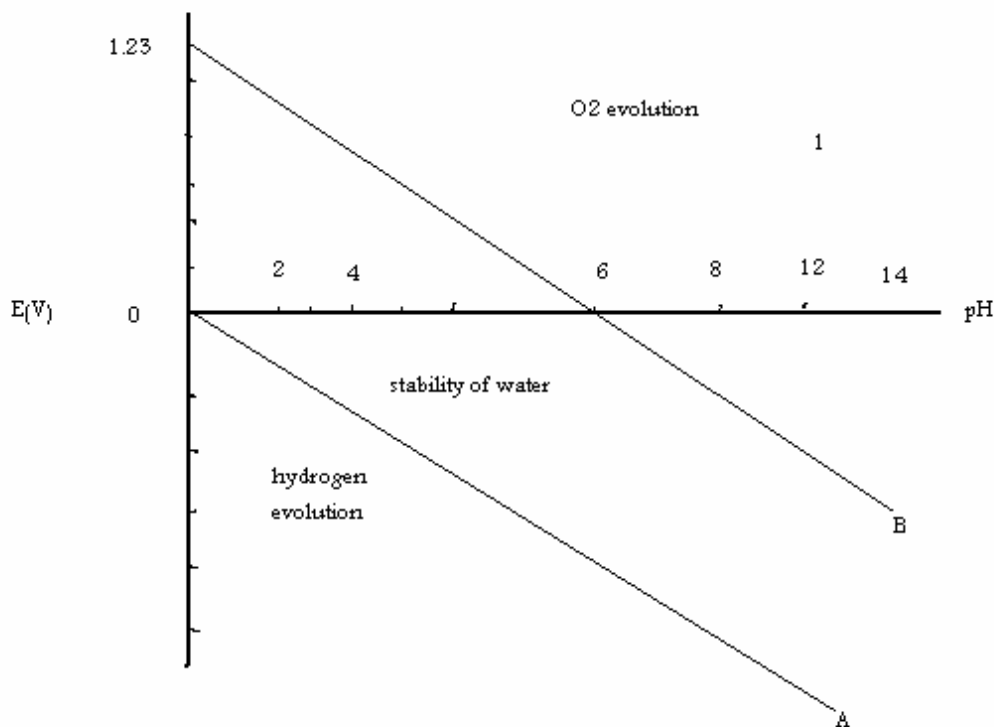
b)

For hydrogen electrode

$$E = -0.0591 \text{ pH}$$

For oxygen electrode

$$E = 1.23 - 0.0591 \text{ pH}$$



The upper line B- represented the revers- equilibrium potential of oxygen electrode as a function of pH.

The bottom line A- represented the revers – equilibrium potential of hydrogen electrode as a function of pH

The two line have the same slope of -59 mv/pH unit at 27°C

The range potential between the two line determine the rang stability of H₂O in aqueous solution.

The electrode potential in solution of a certain pH is put under potential greater than the line B then O₂ would evolved.

If the electrode potential is put under potential under line A. H₂ gas evolved

Question .3

a-

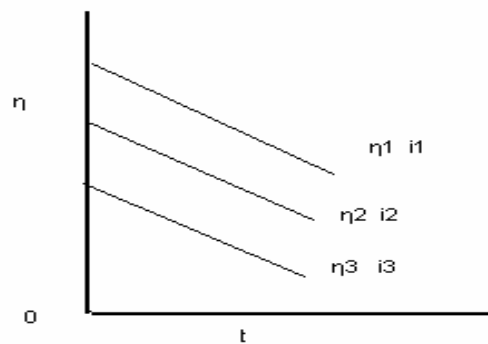
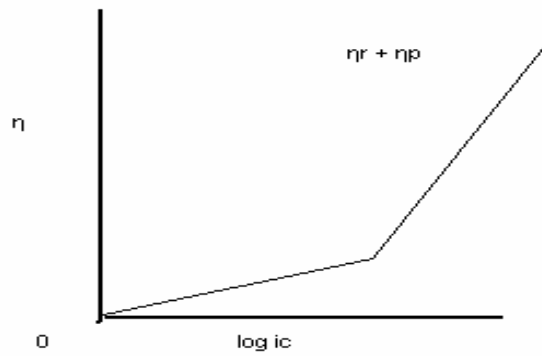
1- Direct method

The value of η is carried out while the electrode is polarized. At

high current densites η_r and η_p are included. And will lead to an upward inflection of Tafel line. In this method the electrode surface must be free from the resistive films, and the tip must be in contact with the electrode surface to minimize η_r and η_p . in this case this method will give good results,

2- in another method the polarizing current is applied and then interrupted after very minute fraction of second and then we follow the decrease of the potential with time. The potential measured is free from η_r and η_p because they decay instantaneously. The straight line is extrapolated to zero time and the values of η at $t=0$ is plotted against $\log i_c$.

3- In the third method various luggen capillaries are placed at different distances from the polarized electrode surfaces. Different potentials, will b recorded at each distance at the same current i_1, i_2, i_3 . The over potential are then plotted against the distance x and the obtained lines are extrapolated to $x=0$, finally the values of η are plotted against $\log i_c$



b- Concentration polarization

Concentration changes near the cathode or the anode are very frequent in the electrolytic processes. Thus near the cathode, the following occurs:

- in the reduction of metal and hydrogen ions, the concentration of the above ions near the cathode decreases than the bulk concentration.

Ex. Reduction of metallic ions as Fe^{+++} , the concentration of Fe^{+++} ions near the electrode surface decreases than the bulk concentration.

Also near the anode the following process occurs:

- in metal dissolution, the concentration of the metallic ions near the electrode, increases than the bulk concentration.

Ex. the oxidation of the metallic ions as Fe^{++} , the concentration of Fe^{++} near the electrode decreases than the bulk concentration

Consider the concentration changes near the cathode. When concentration is plotted against distance as shown in fig .1. Where C_b is the bulk concentration C_e is the concentration near the electrode.

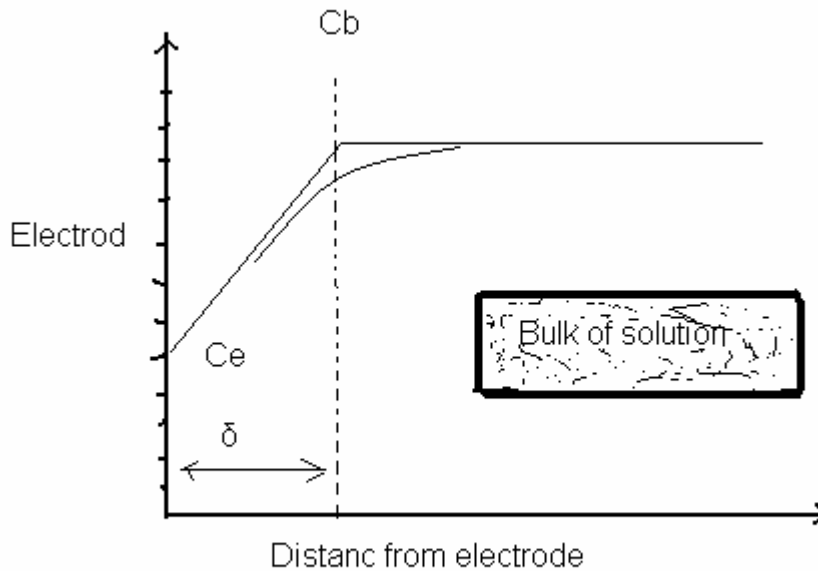


Fig .1.

It is assumed that the concentration reaches the bulk value at a distance from the electrode surface. This distance is the thickness of the layer through which the ions diffuse (from higher concentration C_b to lower concentration C_e). The distance is usually termed the thickness of the diffusion layer. The rate of diffusion is directly proportional to the concentration difference ($C_b - C_e$) and inversely proportional to the thickness of the diffusion layer which is Fick's 1st law of diffusion

$$\text{The rate of diffusion} = D^* (C_b - C_e) / \delta$$

Where D^* is the diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$

In case of ionic diffusion, some of the ions are transported towards the electrode by electrolytic transport. If i is the current density, the rate of electrolytic transport is $\alpha i / ZF$ where αi is the amount of electricity

carried by this ions and Z is the valence of the ion .the total rate of diffusion of a certain ionic species is :

$$\text{Rate of diffusion} = D^* (C_b - C_e) / \delta + \alpha i / ZF$$

The total rate of ionic diffusion is also equal to I / nF , where n is the number of electrons involved in the electrode reaction. The above equation becomes.

$$i / nF = D^* (C_b - C_e) / \delta + \alpha i / ZF$$

When the ion is completely deposited on the cathode, $Z = n$, but when the ion is only reduced at the cathode from higher valance to lower one, n is not equal to Z

Ex. The reduction of Fe^{+++} to Fe^{++} , $n = 1$ while Z for Fe^{+++} is 3

Consider for the simplicity the case when $Z = n$ the above equation become

$$i / nF - \alpha i / nF = D^* (C_b - C_e) / \delta$$

$$i / nF(1 - \alpha) = D^* (C_b - C_e) / \delta$$

Or

$$i = nF D^* (C_b - C_e) / \delta t = k (C_b - C_e)$$

Where $t = (1 - \alpha)$ = transport no. of all ions other than the one deposited or reduced . it is seen that I increases when $(C_b - C_e)$ increases. This don at constant C_b , by decreasing C_e . The maximum value of I , is therefore reached when $C_e = 0$. thus

$$i_1 = k C_b$$

Where i_1 represents the maximum current corresponding to the maximum rate of diffusion of a particular ion and termed the limiting current, the electrode potential governed by the rat of diffusion. The

potential E of the polarized electrode is equal to the reversible potential of this electrode when it inserted in a solution concentration C_e . Thus

$$E_{irr} = E_0 + RT/ZF \ln C_e$$

The potential of E_r of the reversible electrode equal to

$$E_r = E_0 + RT/ZF \ln C_b$$

From above two equations the concentration polarization η_c is given by

$$\eta_c = E_{irr} - E_r = RT/ZF \ln C_e / C_b$$

Where $C_e / C_b = i_1 - i / i_1 = k C_b - i / k C_b$

Hence

$$\Rightarrow \eta_c = RT/ZF \ln i_1 - i / i_1 = RT/ZF \ln k C_b - i / k C_b$$

c-

$$a = 2.303 RT/\alpha F \log i_0 = 0.0591/\alpha \log i_0$$

$$b = 2.303 RT/\alpha F = 0.0591/\alpha$$

$$0.119 = 0.0591/\alpha$$

$$\Rightarrow \alpha = 0.4966 \approx 0.5$$

$$1.54 = 0.0591/0.4966 \log i_0$$

$$1.54 = 0.119 \log i_0$$

$$\log i_0 = 12.94$$

$$\Rightarrow i_0 = 10^{12.94} \text{ Amp.}$$

With my best wishes
Dr. Mohamed Mohamed El- rabiei