Chemistry Department	***Examination of***	***Date: 13/1/2019***
Faculty of Science	***Electrochemistry***	
Benha University.	***(Chem. 234) 2^{nd} level***	***Time: 2 hrs***

Answer the following questions:

I-Choose the right answer of the following: (50 marks)

1- In electrolytic cells:

a- The chemical energy is converted to electrical energy.

b- The electrical energy is converted to chemical energy.

C- The electrical energy is converted to heat energy.

2- For the electrochemical reaction: $Sn^{2+}_{aq} + 2Ag^{+}_{aq} = Sn^{4+}_{aq} + Ag_s$

$E^o_{Sn^{4+}/Sn^{2+}} = 0.15V$ and $E^o_{Ag+/Ag} = 0.8V$. The equilibrium constant is:

a- $9.6x10^{21}$ b- $8.4x10^{25}$ c- $6.4x10^{18}$

3- In amalgam concentration cell:

a- The anode is the electrode of low concentration.

b- The cathode is the electrode of low concentration.

c- The cathode is the electrode of high concentration.

4- In allotropic cells:

a- The electrode which made of metastable modification is the anode.

b- The electrode which made of metastable modification is the cathode.

c- The electrode which made of stable modification is the anode.

5- The standard potential for the Daniel cell: $Cu^{2+}_{aq} + Zn_s = Cu_s + Zn^{2+}_{aq}$

at 25 ^oC is 1.1V. The standard free energy of the cell is:

a- -300.5 kJ/mol b- -212.3 kJ/mol c- 212.3 kJ/mol

6- In the reduction electromotive series:

a- The metal above acts as cathode to that in below.

b- The metal below acts as cathode to that in above .

c- The metal below acts as anode to that in above .

7- In galvanic cells the salt bridge:

a- Prevent only mechanical mixing of the solutions.

a- Eliminates the diffusion potential and prevents the electrolyte mixing.

b- Derives free electrons from one halfcell to the other.

8- Consider a galvanic cell with the following reaction:

$$Cd^{2+}_{aq} + Zn_s = Cd_s + Zn^{2+}_{aq}$$

The potential of the cell is 0.36 V. If the E^o of the zinc electrode is = 0.76 the E^o of the cadmium electrode is: .

a- - 1.12 V b- - 0.4 V c- 0.4 V

9- In the Leclanche cell, the cathodic reaction is:

a- $2MnO_{2(s)} + 2NH_{4\,(aqu)} = Mn_2O_{3\,(s)} + 2NH_{3\,(aqu)} + H_2O_{(l)} + 2\,e$

b- $2MnO_{2(s)}$ + $2NH_{4\,(aqu)}$ + H_2O + 2 e = $Mn_2O_{3\,(s)}$ + $2NH_{3\,(aqu)}$ + $H_2O_{(l)}$

c- $2MnO_{2(s)}$ + $2NH_{4\,(aqu)}$ + 2 e = $Mn_2O_{3\,(s)}$ + $2NH_{3\,(aqu)}$ + H_2O **(•)**

10- In the concentration cell of the second kind:

a- The anode is that immersed in lower electrolyte concentration.

b- The anode is that immersed in higher electrolyte concentration.

c- The cathode is that immersed in lower electrolyte concentration.

11) When a rode of zinc metal is immersed in 1.0 M $CuSO_4$:

a- The $[Cu^{2+}]$ increases. b- The $[Cu^{2+}]$ decreases.

b- No change occurs. $E^o_{Zn/Zn^{2+}}$ = - 0.76 V, $E^o_{Cu/Cu^{2+}}$ = 0.34 V

12) In an electrochemical cell, electrons travel from:

a- The anode to the cathode through the external circuit. **(•)**

b- The anode to the cathode through the salt bridge.

c- The cathode to the anode through the external circuit.

13) The concentration cells of the first kind is defined as:

a) Those which consist of two electrodes of the same material but differ in activities, immersed in the same electrolyte.

b) Those which consist of two electrodes of the same material but differ in activities, immersed in two different electrolytes.

c) Those which consist of two electrodes of different materials immersed in the same electrolyte.

14- Liquid junction potential occurs in:

a) Allotropic cells. b) Concentration cells of the first kind.

c) Concentration cell of the second kind.

15- The mathematical expression of Nernst equation is given by:

a) $E = {}^oE + RT/ZF \ln a_{Ox} / a_{Red}$

b) $E = {}^oE - RT/ZF \ln a_{Ox} / a_{Red}$

c) $E = {}^oE + ZF/RT \ln a_{Ox} / a_{Red}$

16- In gravitational cells:

a- The electrode of greater height has higher free energy act as anode.

b- The electrode of greater height has lower free energy act as anode.

c- The electrode of lower height has higher free energy act as cathode.

17- The relation between ΔG and ΔG^o is given by:

a) $\Delta G = \Delta G^o + RT \ln K_{eq}$ b) $\Delta G = \Delta G^o - RT \ln K_{eq}$

c) $\Delta G = \Delta G^o + RT \ln Q$

18- The dissolution of metals will occur spontaneously if:

a) ΔG has +ve value. b) ΔG has –ve value.

c) ΔG equals to zero.

19- In standard hydrogen electrode, the standard potential E^O depends on

a) The concentration of H^+ ion in the solution.
b) The pressure of the hydrogen gas.
c) Both the H^+ ion concentration and pressure of hydrogen gas.

20- Mercury If $E^o_{Ag^+/Ag} = 0.8V$ and $E^o_{AgI/Ag} = -0.15$ V, the solubility product of AgI is:

a- $8.51x10^{-17}$ b- $8.51x10^{17}$ c- $8.51x10^{-20}$

21- Consider a galvanic cell with the following reaction:

$Cu_s + 2 Fe^{3+}_{aq} = Cu^{2+}_{aq} + 2 Fe^{2+}_{aq}$

$[Fe^{3+}] = 1x10^{-4}$ M, $[Cu^{2+}] = 0.25$ M, $[Fe^{2+}] = 0.2$ M

$E^o_{Cu/Cu^{2+}} = 0.34$ V, $E^o_{Fe^{3+}/Fe^{2+}} = 0.77$ V

The potential of the cell is:

a- 0.25V b- -0.25 V c- 0.61 V

22- In the reduction 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.

23- For the following redox reaction, the oxidation of Mn changes from:

$MnO_4^- + 8 H^+ + x e = Mn^{2+} + 4H_2O$

a- 7 to 4 b- 6 to 2 c- 7 to 2

24- For an electrochemical reaction at equilibrium:

a) $\Delta G = \Delta G^o$ b) $-\Delta G^o = RT \ln Q$ c) $-\Delta G^o = RT \ln K$

25- The oxidation process is defined as:

a) The process which involves a loss of protons.
b) The process which involves a loss of electrons.
c) The process which involves a gain of electrons.

II- Answer the following questions: (30 marks)

1- Sketch and describe and write the electrode reactions of the Standard Weston cell.
2- Sketch and write the notation and the electrode reaction of calomel electrode **OR** silver / silver chloride electrode.
3- Write a brief account on metal- metal oxide electrode. Illustrate your answer with an example.

Model Answer

Answer of question number I:

1- In electrolytic cells:

a- The chemical energy is converted to electrical energy.

b- The electrical energy is converted to chemical energy. **(•)**

C- The electrical energy is converted to heat energy.

2- For the electrochemical reaction: Sn^{2+}_{aq} + $2Ag^{+}_{aq}$ = Sn^{4+}_{aq} + Ag_s

$E^o_{Sn^{4+}/Sn^{2+}}$ = 0.15V and $E^o_{Ag+/Ag}$ = 0.8V. The equilibrium constant is:

a- $9.6x10^{21}$ (•) b- $8.4x10^{25}$ c- $6.4x10^{18}$

3- In amalgam concentration cell:

a) The anode is the electrode of low concentration.

b) The cathode is the electrode of low concentration. **(•)**

c) The cathode is the electrode of high co6ncentration.

4- In allotropic cells:

a- The electrode which made of metastable modification is the anode. **(•)**

b- The electrode which made of metastable modification is the cathoede.

c- The electrode which made of stable modification is the anode.

5- The standard potential for the Daniel cell: Cu^{2+}_{aq} + Zn_s = Cu_s + Zn^{2+}_{aq}

at 25k is 1.1V. The standard free energy of the cell is:

a- 300.5 kJ/mol b- - 212.3 kJ/mol **(•)** c- 212.3 kJ/mol

6- In the reduction electromotive series:

a- The metal above acts as cathode to that in below.

b- The metal below acts as cathode to that in above . **(•)**

c- The metal below acts as anode to that in above .

7- In galvanic cells the salt bridge:

a- Prevent only mechanical mixing of the solutions.

b- El iminates the diffusion potential and prevents the electrolyte mixing. **(•)**

c- Derives free electrons from one half-cell to the other.

8- Consider a galvanic cell with the following reaction:

Cd^{2+}_{aq} + Zn_s = Cd_s + Zn^{2+}_{aq}

The standard potential of the cell is 0.36 V. If the E^o of the zinc electrode is - 0.76 V, the E^o of the cadmium electrode is: .

a- 1.12 V b- - 0.4 V **(•)** c- 0.4 V

9- In the Leclanche cell, the cathodic reaction is:

a- $2MnO_{2(s)}$ + $2NH_{4\,(aqu)}$ = $Mn_2O_{3\,(s)}$ + $2NH_{3\,(aqu)}$ + $H_2O_{(l)}$ + 2 e

b- $2MnO_{(s)}$ + $2NH_{4\,(aqu)}$ + 2 e = $MnO_{2\,(s)}$ + $2NH_{3\,(aqu)}$ + $H_{2(g)}$

c- $2MnO_{2(s)}$ + $2NH_{4\,(aqu)}$ + 2 e = $Mn_2O_{3\,(s)}$ + $2NH_{3\,(aqu)}$ + $H_2O_{(l)}$ **(•)**

10- In the concentration cell of the second kind:

a-The anode is that immersed in lower electrolyte concentration. **(•)**

b-The anode is that immersed in higher electrolyte concentration.

c-The cathode is that immersed in lower electrolyte concentration.

11- When a rode of zinc metal is immersed in 1.0 M $CuSO_4$:

a- The $[Cu^{2+}]$ increases. b- The $[Cu^{2+}]$ decreases. **(•)**

c- No change occurs. $E^o_{Zn/Zn^{2+}}$ = - 0.76 V, $E^o_{Cu/Cu^{2+}}$ = 0.34 V

12- In an electrochemical cell, electrons travel from:

a- The anode to the cathode through the external circuit. **(•)**

b- The anode to the cathode through the salt bridge.

c- The cathode to the anode through the external circuit.

13- The concentration cell of the first kind is defined as:

a- Those which consist of two electrodes of the same material but differ in activities, immersed in the same electrolyte. **(•)**

b- Those which consist of two electrodes of the same material but differ in activities, immersed in two different electrolytes.

d- Those which consist of two electrodes of different materials immersed in the same electrolyte.

14- Liquid junction potential occurs in:

a) Allotropic cells. b) Concentration cells of the first kind.

c) Concentration cell of the second. **(•)**

15- The mathematical expression of Nernst equation is given by:

a- $E = E^o + RT/ZF \ln a_{Ox} / a_{Red}$ **(•)**

b- $E = E^o - RT/ZF \ln a_{Ox} / a_{Red}$

c- $E = E^o + ZF/RT \ln a_{Ox} / a_{Red}$

16- In gravitational cells:

a- The electrode of greater height has higher free energy act as anode. **(•)**

b- The electrode of greater height has lower free energy act as anode.

c- The electrode of lower height has higher free energy act as cathode.

17- The relation between ΔG and ΔG^o is given by:

a) $\Delta G = \Delta G^o + RT \ln K_{eq}$ b) $\Delta G = \Delta G^o - RT \ln K_{eq}$

c) $\Delta G = \Delta G^o + RT \ln Q$ **(•)**

18- The dissolution of metals will occur spontaneously if:

a- ΔG has + ve value. b- ΔG has – ve value. **(•)**

c- ΔG equals to zero.

19- In standard hydrogen electrode, the standard potential E^O depends on

a- The concentration of H^+ ion in the solution.

b- The pressure of the hydrogen gas.

c- Both the H^+ ion concentration and pressure of hydrogen gas. **(•)**

20- If $E^o_{Ag^+/Ag} = 0.8V$ and $E^o_{AgI/Ag} = -0.15$ V, the solubility product of AgI is:

a- $8.51x10^{-17}$ **(•)** b- $8.51x10^{17}$ c- $8.51x10^{-20}$

21- Consider a galvanic cell with the following reaction:

Cu_s + $2 Fe^{3+}_{aq}$ = Cu^{2+}_{aq} + $2 Fe^{2+}_{aq}$
$[Fe^{3+}] = 1x10^{-4}$ M, $[Cu^{2+}] = 0.25$ M, $[Fe^{2+}] = 0.2$ M
$E^o_{Cu / Cu^{2+}} = 0.34$ V, $E^o_{Fe^{3+} / Fe^{2+}} = 0.77$ V
The potential of the cell is:

a- 0.25V **(•)** b- - 0.25 V c- 0.61 V

22- In the reduction 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

23- For the following redox reaction, the oxidation of Mn changes from:

$MnO_4^- + 8 H^+ + x e = Mn^{2+} + 4H_2O$

a- 7 to 4 b- 6 to 2 c- 7 to 2 **(•)**

24- For an electrochemical reaction at equilibrium:

a) $\Delta G = \Delta G^o$ b) $- \Delta G^o = RT \ln Q$ c) $- \Delta G^o = RT \ln K$ **(•)**

25- The oxidation process is defined as:

a) The process which involves a loss of protons.

b) The process which involves a loss of electrons. **(•)**

c) The process which involves a gain of electrons.

Answer of question No. II 1:

Standard Weston cell is a simple cell has extremely stable emf and has a small temperature coefficient. The electrode reaction occurs at the anode is:

$$Cd = Cd^{2+} + 2 e$$

Whereas that occurs at the cathode is:

$$Hg_2SO_4 + 2 e = 2 Hg + SO_4^{2-}$$

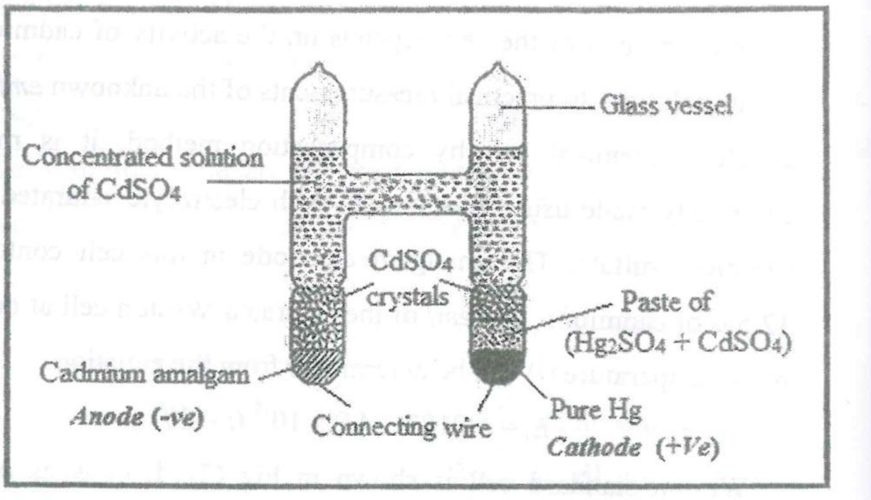
The overall reaction in the cell may be written as:

$$Cd + Hg_2SO_4 = Cd^{2+} + SO_4^{2-} + 2 Hg$$

Applying the Nernst equation, the emf of the Weston cell is given by the equation:

$$E_{cell} = E^o_{cell} + RT/ZF \ln a_{Cd^{2+}} a_{SO4^{2-}}$$

Thus, the emf of the cell depends on the activity of cadmium sulphate in solution. The amalgam electrode in this cell contains 12.5% of cadmium. Weston standard cell is shown in the following figure. It consists of H-shaped glass vessel, each leg being 2.5 cm in diameter containing concentration solution of cadmium sulfate in the upper part, then crystals of of cadmium sulfate, paste of mercurous sulfate and cadmium sulfate over them. Mercury at the bottom of one leg (cathode) and crystals of cadmium sulfate and cadmium amalgam at the bottom of second leg (anode). The two limbs of the vessel are sealed. Cadmium sulfate solution acts as an electrolyte, mercury acts as the positive electrode (cathode) whereas, cadmium amalgam acts as the negative electrode (anode) and cadmium sulfate acts as the electrolyte. Crystals of cadmium sulfate are put in the cell in order to keep the electrolyte saturated. The connections of the cell into the external circuit are made by platinum wire sealed into the glass.



Answer of question No. II 2:

Calomel electrode:

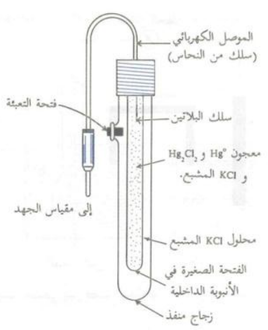
calomel electrode is the most frequently used reference electrode in the laboratory. It consists of a pool of mercury covered with a layer of mercurous chloride (calomel) and immersed in solution of potassium chloride acting as the electrolyte as shown in the following figure. The electric contact to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

$$Hg_2Cl_2 \quad + \quad 2\,e \quad = \quad Hg \quad + \quad 2\,Cl^-$$

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

$$E \quad = \quad E^o \quad - \quad 0.0591 \; \log \; [Cl^-]$$

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.



Silver-silver chloride electrode:

This electrode can be represented as: $AgCl_{(s)}, Ag / Cl^{-}_{(aqu)}$

The following electrochemical reaction takes place:

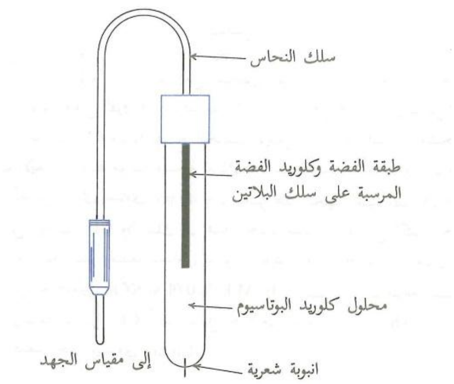
$$AgCl_{(s)} + e = Ag_{(s)} + Cl^{-}_{(aqu)}$$

The potential of the electrode can be given using Nernst equation:

$$e_{Cl^-/AgCl} = e^{o}_{Cl^-/AgCl} - RT/ZF \ln a_{Cl^-}$$

$$e_{Cl^-/AgCl} = 0.2224 - 0.0591 \ln a_{Cl^-}$$

The electrolyte used in this reference electrode is hydrochloric acid. Ag/ AgCl electrode can be used in calculation of the solubility product of silver chloride salt.



Answer of question No. II 3:

a) Metal-metal oxide electrode:

This group of electrodes is interested because the metal hydroxide anions play the role of sparingly soluble compound. Examples of this kinds are the antimony-antimony oxide electrode and the mercury-mercuric oxide electrode. The antimony-antimony oxide cab be represented as:

$$OH^{-} / Sb_2O_{3,} Sb$$

The equations for the electrode reactions are:

$$Sb_2O_{3.}\ 3H_2O = 2\ Sb^{3+} + 6\ OH^{-} + 6\ e$$

$$2\ Sb^{3+} + 6\ e = 2\ Sb_2O_3$$

The overall reaction is: $Sb_2O_3 .\ 3\ H_2O + 6\ e = 2\ Sb + 6\ OH^{-}$

Applying Nernst equation to calculate the electrode potential assuming that the activities of the metal and its oxide as well as that of water are constants we have:

$$e_{Sb} = e^{o}_{Sb} - RT/6F \ln (a_{OH^-})^6$$

$$e_{Sb} = e^{o}_{Sb} - RT/F \ln a_{OH^-} = e^{o}_{Sb} - 0.0591 \log a_{OH^-}$$

substituting $a_{OH^-} = K_w / a_{H^+}$ $(K_w = a_{OH^-} \times a_{H^+})$

$$e_{Sb} = e^{o}_{Sb} - 0.0591 \log a_{OH^-} = e^{o}_{Sb} - 0.0591 \log k_w / a_{H^+}$$

$$= e^{o}_{Sb} - 0.0591 \log k_w / a_{H^+} = (e^{o}_{Sb} - 0.0591 \log 10^{-14}) + 0.0591 \log a_{H^+}$$

$$= (e^{o}_{Sb} - 0.0591 \log 10^{-14}) + 0.0591 \log a_{H^+}$$

$$= \text{constant} - 0.0591\ pH \qquad (-\log a_{H^+} = pH)$$

The antimony-antimony oxide electrode can not be employed as a reference electrode because of the instability of its surface oxide, it finds applications as an indicator electrode for approximate pH measurements in moderately acidic and neutral solutions.

Using the same procedure results in the following equations for mercury-mercuric oxide electrode we have:

$$e_{Hg} = e^{o}_{Hg} - RT/2F \ln (a_{OH^-})^2$$

$$e_{Hg} = e^{o}_{Hg} - RT/F \ln a_{OH^-}$$

$$e_{Hg} = e^{o}_{Hg} - 0.0591 \log a_{OH^-}$$

$$e_{Hg} = \text{costant} + 0.0591 \log a_{H^+}$$

$$e_{Hg} = \text{costant} - 0.0591 \log pH$$

The mercury-mercuric oxide electrode is recommended only for pH solutions > 7 because mercury oxides are perceptibly soluble in acidic solutions. The overall electrode reaction is:

$$HgO + H_2O + 2e = Hg + 2OH^-$$

The mercury/ mercuric oxide electrode can be represented as: OH^- / HgO, Hg