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| مسابقة في مادة الكيمياء | **الاسم:** |
| المدة ساعتان | **الرقم:** |

**This Exam Includes Three Exercises. It Is Inscribed on 4 Pages Numbered From 1 to 4. The Use of A Non-programmable Calculator is Allowed.**

**Answer The Three Following Exercises:**

## First Exercise (7 points)
## Acid-Base Reaction

The label of a bottle containing a commercial hydrobromic acid solution shows, among others, the following indications:

46 % by mass of HBr; density: 1.47 $g.mL^{-1}$.

The aim of this exercise is to perform an acid-base study of a dilute aqueous hydrobromic acid solution.

**Given**:

- M( HBr ) = 81 $g.mol^{-1}$
- pKa ($NH_4^+/NH_3$) = 9.2

### 1- Dilution of the Commercial Solution

1.1- Show that the molar concentration of the commercial solution is $C_0 = 8.35\ mol.L^{-1}$.

1.2- Describe the experimental procedure to be followed in order to prepare 1 L of a solution (S) by diluting the commercial solution 200 times .

1.3- The pH of the solution (S) is equal to 1.38

1.3.1- Show that HBr is a strong acid.

1.3.2- Write the equation of its reaction with water.

### 2- Titration of an Aqueous Ammonia Solution.

The solution (S) is added, progressively, into a beaker containing a volume $V_b = 10.0$ mL of an ammonia solution ($NH_3$) of concentration $C_b$, in the presence of an appropriate colored indicator. The volume of the acid added to reach equivalence is $V_{aE}$= 12ml

2.1- Write the equation of the titration reaction.

2.2- Justify, based on the chemical species present at equivalence, the acid character of this medium.

2.3- Show that the concentration of the ammonia solution is $C_b = 5.0\times10^{-2}\ mol.L^{-1}$.

2.4- Calculate the volume of ammonia gas needed to prepare 1 L of the ammonia solution of concentration $C_b$, knowing that the molar volume of a gas is $V_m = 24\ L.mol^{-1}$.

### 3- Preparation of a Buffer Solution

Determine the volume $V_1$ of the solution (S) that should be added to a volume $V_2 = 50$ mL of the ammonia solution of concentration $C_b$ in order to prepare a buffer solution of pH = 9.0

## Second Exercise (6 points)
## Synthesis of an Ester

Available are two flasks: one containing glacial (pure) ethanoic acid and the other contains a liquid of a pure saturated noncyclic chain organic compound (A).
The aim of this exercise is to identify the organic compound (A) then to study its reaction with ethanoic acid.

### 1- Identification of the Family of (A)

In order to identify the chemical family of the compound (A), the experiments listed below are carried out:

| Number of the experiment | Experiment | Result of the experiment |
|---|---|---|
| 1 | (A) + sodium metal | Hydrogen gas release. |
| 2 | Heating a mixture of : (A)+ thionyl chloride ($SOCl_2$) | Formation of an organic compound (B) accompanied with the release of two gases. |

Moreover, a study of the compound (B) shows that the molecule of the compound (B) contains only carbon, hydrogen and chlorine.

1.1- Interpret the result of experiment 1.
1.2- Deduce from the experiment 2, the possible chemical families of the compound (B).
1.3- Show that the compound (A) is an alcohol of general formula $C_xH_{2x+2}O$.

### 2- Esterification Reaction

A mixture of 0.5 mol of ethanoic acid and of 0.5 mol of the compound A is heated. At equilibrium, a quantity of 0.3 mol of an ester E of molecular formula $C_6H_{12}O_2$ is obtained.

**Given:**

The equilibrium constant K, associated with the equation:

$$RCOOH_{(l)} + R'OH_{(l)} \rightleftarrows RCOOR'_{(l)} + H_2O_{(l)}$$

is equal to 4.12 if the alcohol is primary and to 2.25 if the alcohol is secondary.

2.1- Determine the molecular formula of the alcohol (A).
2.2- Write the possible condensed structural formulas of the ester (E).
2.3- Show that the equilibrium constant of the equilibrium realized above is equal to 2.25
2.4- Identify the alcohol (A) and name the ester (E).

2.5- Represent, according to Cram, the two enantiomers of the alcohol (A).

## Third Exercise (7 points)
## Oxidation of Iodide Ions

A solution (S) is prepared by mixing a volume 100 mL of a potassium iodide solution($K^+ + I^-$) of concentration $C_1 = 0.80$ mol.L $^{-1}$ with a volume 100 mL of sodium peroxydisulfate solution ($2\ Na^+ + S_2O_8^{2-}$) of concentration $C_2 = 0.20$ mol.L$^{-1}$.

A brown color is observed which intensifies with time representing a complete reaction that takes place according to the following equation:

$$S_2O_8^{2-} + 2\ I^- \rightarrow 2\ SO_4^{2-} + I_2$$

At different time intervals, a precise volume of the solution (S) is taken and the iodine formed is titrated,in the presence of starch solution, using a sodium thiosulfate solution($2\ Na^+ + S_2O_3^{2-}$) according to the equation:

$$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$$

**Given**:

- $Fe^{2+}$ is a catalyst for the reaction of formation of iodine.
- M ($Na_2S_2O_3.\ 5\ H_2O$) = 248 g.mol$^{-1}$

### 1- Preparation of Sodium Thiosulfate Solution

The sodium thiosulfate solution, used to titrate iodine, is prepared by dissolving a mass m = 25.0 g of the hydrated powder ($Na_2S_2O_3.5H_2O$) in distilled water in order to have a solution of volume V = 500.0 mL.

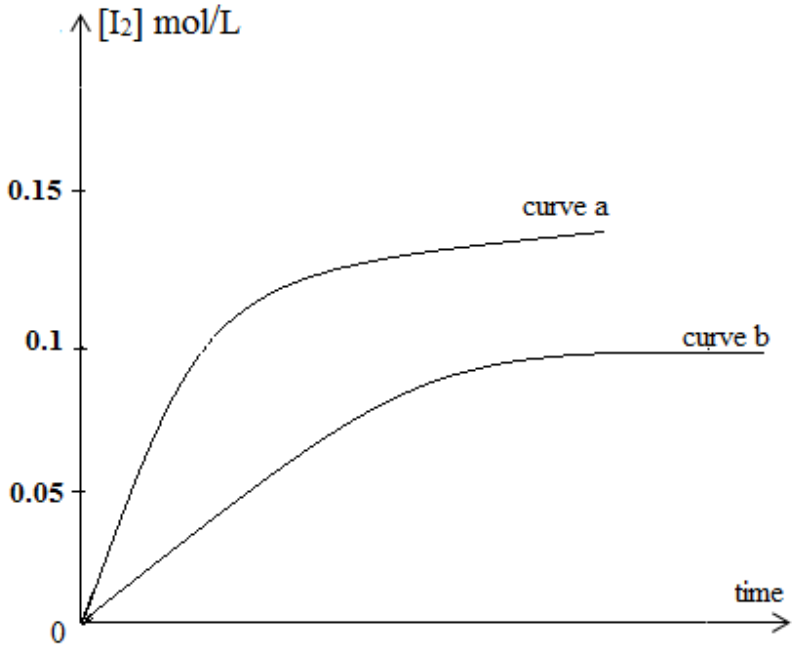
1.1- List the essential materials needed to carry out this preparation.
1.2- Calculate the molar concentration C of this solution.

### 2- Titration of Iodine

2.1- Propose, by justifying, an experimental way to stop the formation of iodine in each volume taken before carrying out titration.
2.2- Specify the color change at equivalence.

### 3- Kinetic Study

3.1- Given the shapes of the two curves a and b.
Choose the one that corresponds to the change of the iodine concentration, in the solution S, versus time: $[I_2] = f(t)$.Justify




3.2- The experimental study shows that this reaction ends at t = 70 min.

3.2.1- Define the half- life time of the reaction

3.2.2- Choose, by justifying, among the three following proposals, the appropriate one for the half-life time :

$t_{1/2} = 35$ min ; $t_{1/2} > 35$ min ; $t_{1/2} < 35$ min.

3.3- The interval of time $\Delta t$ denotes the end time of reaction for each of the reacting mixtures considered in the table below:

| Reacting mixture | Temperature of the mixture | $\Delta t$ |
|---|---|---|
| Mixture (1) :a volume V of solution (S) | $40^{o}C$ | $\Delta t_1$ |
| Mixture (2) :a volume V of solution (S) + few mL of a solution of $Fe^{2+}$ ions (without a noticeable change in volume). | $20^{o}C$ | $\Delta t_2$ |

Verify whether $\Delta t_1$ and $\Delta t_2$ could be compared.