**This Exam Includes Three Exercises. It is Inscribed on Four Pages Numbered From 1 to 4.**
**The Use of a Non- Programmable Calculator Is Allowed.**
**Answer The Three Following Exercises.**

## First Exercise (7 points)
## Identification of Organic Compounds

The aim of this exercise is to identify two organic compounds: a liquid (A) of molecular formula $C_2H_XO$ and a saturated non- cyclic chain primary monoamine (B) in order to study their action on ethanoic acid.

### 1- Identification of Compound (A)

1.1- Write the possible condensed structural formulas of the organic compounds of molecular formula $C_2H_XO$.
1.2- In order to identify (A), the two experimental activities below are carried out:

| Number of the activity | Experimental activity | Result |
|---|---|---|
| 1 | An excess of a potassium permanganate solution is added to the compound (A) in acidic medium. | A compound (C) is obtained which, dissolved in water, gives a solution with a pH clearly less than 7 |
| 2 | A mixture of (A) and thionyl chloride is heated gently. | A gaseous mixture evolves and a chlorinated organic compound is formed. |

Consider each one of these two results and specify if it allows identifying the organic compound (A).

### 2- Identification of the Compound (B)

**Given:**
Molar mass in $g.mol^{-1}$ : M(H) = 1 ; M(C) = 12 and M(N) = 14

A mass m = 3.70 g of the amine (B) is dissolved in distilled water in such a way to obtain 500 mL of a solution (S).
A volume $V_1$ = 20.0 mL of this solution is titrated with a hydrochloric acid solution of concentration $C_2 = 0.20\ mol.L^{-1}$ in the presence of an appropriate colored indicator.
The color change of this colored indicator is observed when a volume $V_E$ = 10.2 mL of the acid solution is added.
The equation of the titration reaction is:

$$R-NH_2 + H_3O^+ \rightarrow R-NH_3^+ + H_2O$$

2.1- Determine the molar concentration $C_1$ of the solution (S).
2.2- Deduce the molar mass of the amine (B).
2.3- Show that its molecular formula is $C_4H_{11}N$.
2.4- Write the possible condensed structural formulas of (B).
2.5- Identify (B) knowing that its carbon chain is straight (non branched) and does not possess any asymmetric carbon.

**3- Action of the Ethanoic Acid on (A) and (B)**

The following two experiments are carried out:
Experiment 1: A mixture of ethanoic acid and the compound (A) is heated; a fruity odor ester is formed.
Experiment 2: A mixture of ethanoic acid and compound (B) is heated; an amide is formed.

3.1- Give two characteristics of the reaction carried out in the experiment 1.
3.2- Identify the amide obtained in the experiment 2.
3.3- Write the condensed structural formula of an organic compound that could replace the ethanoic acid in each of the two experiments 1 and 2. Name it.

## Second Exercise ( 7 points)
## Acid-Base Reactions

Four flasks are numbered and an aqueous solution of one of the species below is introduced into each one of these flasks.

| Number of the flask | Chemical species | |
|---|---|---|
| | Name | Formula |
| 1 | Hydrogen fluoride | HF |
| 2 | Sodium methanoate | HCOONa |
| 3 | Ammonia | $NH_3$ |
| 4 | Ammonium chloride | $NH_4Cl$ |

**These solutions have the same molar concentration C.**
**Given :**

-

| Acid / base pair | $NH_4^+ / NH_3$ | $HF / F^-$ | $HCOOH / HCOO^-$ |
|---|---|---|---|
| $pK_a$ | 9.2 | 3.2 | 3.8 |

- Sodium methanoate and ammonium chloride are both ionic compounds highly soluble in water.

**1-** Classify the above four solutions as acidic and basic solutions.

**2- Preparation of the Solution of the Flask 3**

The solution in the flask 3 of molar concentration C, has been prepared starting from a commercial ammonia solution of which the label shows the following indications:
Percentage by mass = 25% density: d = 0.91 $g.mL^{-1}$ $M(NH_3) = 17\ g.mol^{-1}$
A volume $V_o = 1.5$ mL of this commercial solution is taken and distilled water is added to this volume in such a way to obtain a solution of volume V = 2.0 L.

2.1- Determine the molar concentration $C_o$ of the commercial solution.
2.2- Show that the molar concentration $C = 1.0\times10^{-2}\ mol.L^{-1}$.

2.3- Choose, from the following glassware, those that are essential for the preparation of the solution in the flask 3:
2 mL volumetric pipet, 2 mL graduated cylinder, 2 mL graduated pipet, 2 L graduated cylinder and 2 L volumetric flask.

**3- Study of the Solution of the Flask 1**

3.1- Write the equation of the reaction between HF and water.
3.2- Determine the degree of ionization of HF in the solution of the flask 1.
($[F^-]$ is neglected compared to the concentration C)

**4- Mixture of Two Solutions**

A volume $V_1$ = 40 mL of the solution of the flask 1 ( HF solution) is mixed with a volume $V_2$ = 30 mL of the solution of the flask 3 ($NH_3$ solution). The equation of the reaction that takes place is the following:

$$HF + NH_3 \rightarrow F^- + NH_4^+$$

4.1- Justify that this reaction is complete.
4.2- Specify the limiting reactant.
4.3- Deduce the pH of the obtained mixture.

**Third Exercise (6 points)**
**Kinetic of the Oxidation of 2-propanol**

The oxidation of 2-propanol with permanganate ions in acidic medium is slow and complete.
The equation of this reaction is the following:

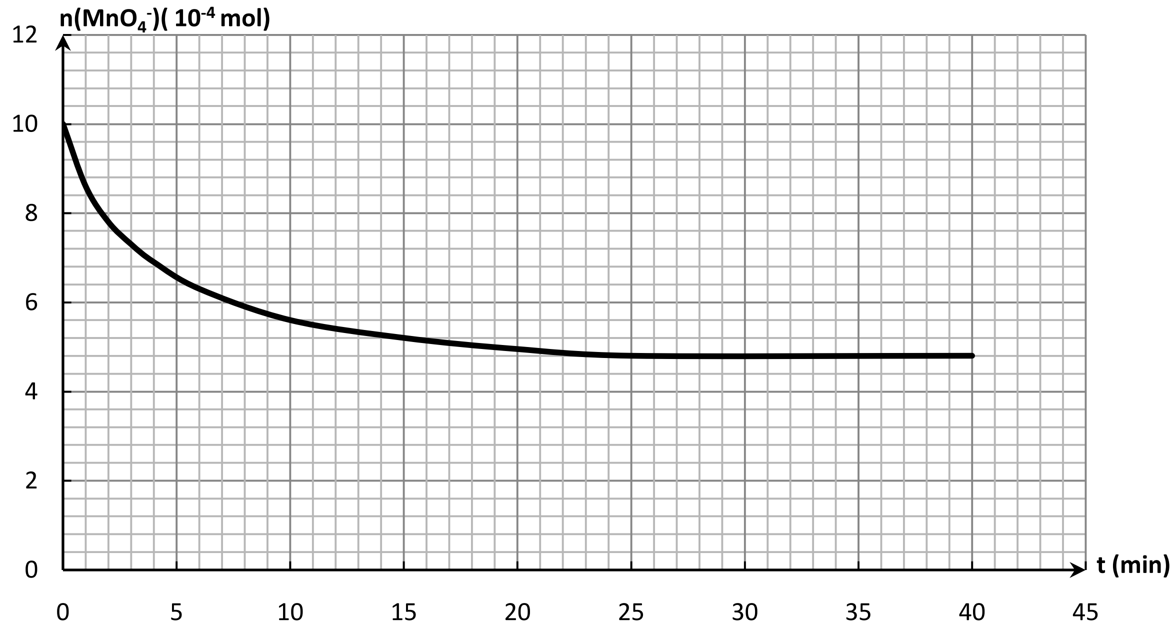
$$5\ C_3H_8O + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ C_3H_6O + 2\ Mn^{2+} + 8\ H_2O \quad \text{(Reaction 1)}$$

The kinetic study of this transformation is carried out by titrating the permanganate ions remaining, at each instant of time t, with an iron (II) sulfate solution.

**Procedure**

- Available are eight beakers, each containing a volume $V_o$ = 10 mL of an acidified potassium permanganate solution of concentration $C_o$ = 0.10 mol.$L^{-1}$ (excess of sulfuric acid solution)
- At the instant of time t = 0, two drops of 2-propanol are added to the content of each beaker which is stirred using magnetic stirrer.
- At an instant of time $t_1$ = 1 min, one of these beakers is immersed rapidly in an icy-water bath and the remaining permanganate ions are titrated with an iron (II) sulfate solution.
- The preceding step is repeated with the other beakers at the different instants of time indicated in the following graph below.

The different titrations carried out allow to plot the curve below representing the variation in the number of moles of permenganate ions remaining as a function of time.




## 1- Identification of The Compound $C_3H_6O$

1.1- Specify the chemical family of the organic compound obtained in the reaction 1.
1.2- Identify this organic compound.

## 2- Preliminary Study

2.1- Based on the curve given above, deduce that the 2-propanol is the limiting reactant in the reaction 1.

2.2- Establish the following relation: $n\,(C_3H_6O)_t = \frac{5}{2}\,[\,1.0\times10^{-3} - n\,(MnO_4^-)_t\,]$.

Where $n\,(C_3H_6O)_t$ is the number of moles of $C_3H_6O$ at t and $n\,(MnO_4^-)_t$ is the number of moles of $MnO_4^-$ remaining at the same instant of time t, in each one of the eight beakers.

2.3- Indicate the aim of placing each beaker in an icy-water bath before carrying out the titration.

## 3- Kinetic Study

3.1- Calculate the average rate of disappearance of $MnO_4^-$ within the time interval: [0-10 min].

3.2- One of the following values represents the half life time of the oxidation reaction of 2-propanol: t = 25 min, t = 12.5 min and t = 2.5 min.
Choose the appropriate value. Justify.

3.3- The procedure realized above is carried out again but with one single change: four drops of 2-propanol are added to the content of each beaker (without noticeable change in the volume $V_o$)
Verify whether the number of moles of permanganate ions remaining at t = 6 min is less, equal or greater than $6.3\times10^{-4}$ mol.

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الدورة العادية 2013

## اسس تصحيح مسابقة الكيمياء

# First Exercise (7 points)
# Identification of Organic Compounds

| Part of the Q | Answer | Mark |
|---|---|---|
| 1.1 | The possible condensed structural formulas are:<br>$CH_3 - CH_2OH$; $CH_3 - CHO$ and $CH_3 - O - CH_3$ | 0.75 |
| 1.2 | 1st result<br>The pH of the aqueous solution of (C) is less than 7 ; (C) is an acid.<br>(C) is obtained by the mild oxidation of (A) ; (A) could be ethanol or ethanal.<br>2nd result :<br>The organic product is chlorinated; a chlorine atom substitutes a hydroxyl group. So (A) is ethanol of formula $CH_3 - CH_2OH$. | 1 |
| 2.1 | At the equivalence point :<br>n ($H_3O^+$) added = n ($R - NH_2$) titrated<br>$C_2 \times V_E = C_1 \times V_1$ ; $C_1 = \frac{C_2 \times V_E}{V_1} = \frac{0.20 \times 10.2}{20} = 0.10 \text{ mol.L}^{-1}$. | 0.75 |
| 2.2 | $M(B) = \frac{m(B) \text{ in } 500 \text{ mL}}{n(B) \text{ in } 500 \text{ mL}} = \frac{3.7}{0.10 \times 0.5} = 74 \text{ g.mol}^{-1}$. | 0.75 |
| 2.3 | (B) is a saturated non cyclic chain monoamime; its general formula is of the form $C_nH_{2n+3}N$.<br>M(B) = 14n +17 = 74, so n = 4. So its molecular formula is $C_4H_{11}N$ | 0.5 |
| 2.4 | The possible condensed formulas of (B) :<br>$CH_3 - CH_2 - CH_2 - CH_2 - NH_2$; $CH_3 - CH_2 - CH(NH_2) - CH_3$; $CH_3 - CH(CH_3) - CH_2 - NH_2$<br>$CH_3 - C(NH_2)(CH_3) - CH_3$ | 1 |
| 2.5 | The straight chain of (B) is non branched and does not contain an asymmetric carbon; (B) is 1- butanamine (of formula $CH_3 - CH_2 - CH_2 - CH_2 - NH_2$). | 0.5 |
| 3.1 | The two characteristics of the reaction carried out in the experiment 1 are: slow and reversible | 0.5 |
| 3.2 | The formula of the amide obtained is : $CH_3 - CO - NH - CH_2 - CH_2 - CH_2 - CH_3$<br>Its name: N-butylethanamide. | 0.75 |
| 3.3 | The compound may have the formula: $CH_3 - C(=O) - O - C(=O) - CH_3$<br>Its name is ethanoic anhydride | 0.5 |

**Second Exercise (7 points)**
**Acid-Base Reactions**

| **Part of the Q** | **Answer** | **Mark** |
|---|---|---|
| 1 | The acidic solutions are: HF solution and ammonium chloride solution.<br>The basic solutions are: sodium methanoate solution and ammonia solution. | 1 |
| 2.1 | The concentration $C_o$ of the commercial solution is :<br>$C_o = \frac{n(NH_3)}{V(solution)}$ ;<br>% by mass = $\frac{m(NH_3)}{m(solution)} \times 100 = 25$ and d (solution) = $\frac{m(solution)}{V(solution)}$ = 0.91g.mL$^{-1}$<br>and $M(NH_3) = \frac{m(NH_3)}{n(NH_3)}$ = 17g.mol$^{-1}$ ;<br>The relation below can be deduced:<br>$C_o = \frac{\%by.mass \times d(solution) \times 10}{M(NH_3)}$ =13.4 mol.L$^{-1}$. | 1.25 |
| 2.2 | During dilution the number of moles of the solute is conserved.<br>$C_o \times V_o = C \times V$ ; $C = \frac{C_o \times V_o}{V} = \frac{13.4 \times 1.5}{2000} = 1.0 \times 10^{-2}$ mol.L$^{-1}$. | 0.75 |
| 2.3 | We must choose 2 mL graduated pipet to take the volume $V_o$ and 2 L volumetric flask to prepare the volume V. | 0.5 |
| 3.1 | The equation of the reaction between HF and water:<br>$HF + H_2O \rightleftarrows F^- + H_3O^+$ | 0.5 |
| 3.2 | $\alpha = \frac{n(HF)dissociated}{n(HF)initial} = \cdots = \frac{[F^-]}{C}$<br><br>$HF + H_2O \rightleftarrows F^- + H_3O^+$<br>Initial state: C, solvent, -, -<br>At equilibrium (obtained solution): $C - C\alpha$, solvent, $C\alpha$, $C\alpha$<br>$K_a = K_{(reaction)} = \frac{[F^-]\times[H_3O^+]}{[HF]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$ = C. $\alpha^2$ ; So $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-3.8}}{10^{-2}}}$ = 0.12 | 1 |
| 4.1 | The reaction constant $K_r$ is :<br>$K_r = 10^{pK_a(NH_4^+/NH_3) - pK_a(HF/F^-)} = 10^{9.2-3.2} = 10^6 > 10^4$; so the reaction is complete. | 0.5 |
| 4.2 | $R(HF) = \frac{n(HF)}{1} = \frac{C \times V_1}{1} = 10^{-2} \times 40 \times 10^{-3} = 4 \times 10^{-4}$<br>$R(NH_3) = \frac{n(NH_3)}{1} = \frac{C \times V_2}{1} = 10^{-2} \times 30 \times 10^{-3} = 3 \times 10^{-4}$<br>$R(NH_3) < R(HF)$ implies $NH_3$ is the limiting reactant. | 0.5 |

| | | |
|---|---|---|
| 4.3 | $HF + NH_3 \rightarrow F^- + NH_4^+$<br>initial state: $4\times10^{-4}$, $3\times10^{-4}$, -, -<br>final state: $4\times10^{-4} - 3\times10^{-4}$, 0, $3\times10^{-4}$, $3\times10^{-4}$<br><br>pH(solution) = $pK_a$ (HF / $F^-$) + log $\frac{[F^-]}{[HF]}$<br><br>with log $\frac{[F^-]}{[HF]}$ = log $\frac{\frac{3\times10^{-4}}{70\times10^{-3}}}{\frac{1\times10^{-4}}{70\times10^{-3}}}$ = log 3<br><br>and pH = 3.2 + log 3 = 3.7 | 1 |

## Third Exercise (6 points)
## Kinetic of The Oxidation of 2-propanol

| Part of the Q | Answer | Mark |
|---|---|---|
| 1.1 | $C_3H_6O$ is produced by the mild oxidation of a secondary alcohol (2-propanol), so this compound belongs to the ketone family. | 0.75 |
| 1.2 | The condensed structural formula of $C_3H_6O$ is : $CH_3 – CO – CH_3$, it is the propanone | 0.75 |
| 2.1 | The oxidation reaction of 2- propanol is complete and the $H^+$ ions are in excess.<br>According to the graph, the end of the reaction is reached (t = 25 min) and $MnO_4^-$ ions are not consumed completly. So 2-propanol is the limiting reactant. | 0.75 |
| 2.2 | $n(C_3H_6O)_t = \frac{5}{2}$ n ($MnO_4^-$) disappeared at t= $\frac{5}{2}$ [ n ($MnO_4^-$) initial - $n(MnO_4^-)_t$ ]<br>$= \frac{5}{2}[(1.0\times10^{-3} - n(MnO_4^-)_t]$ | 0.75 |
| 2.3 | The immersing of the beaker in an icy-water bath blocks the oxidation reaction of<br>2- propanol. | 0.5 |
| 3.1 | The average rate of disappearence of $MnO_4^-$ ions is:<br>$r(MnO_4^-) = -\frac{\Delta(MnO_4^-)}{\Delta t} = -\frac{n(MnO_4^-)_{10\,min} - n(MnO_4^-)_0}{10} = \frac{(10-5.6)\times10^{-4}}{10}$<br>$= 4.4\times10^{-5}$ mol.min$^{-1}$. | 1 |
| 3.2 | t = 25 min and t = 12.5 min could not be the half life time of the reaction since the first one represents the end time of the reaction and the 2nd one is $t_\infty / 2$. thus, $t_{1/2}$ = 2.5 min. | 0.75 |
| 3.3 | The number of moles of 2-propanol increases in the same volume, implies the concentration of 2-propanol has increased. The concentration of 2-propanol is a kinetic factor, as the concentration increases the rate of the reaction increases.<br>In the first case n ($MnO_4^-$) remaining at 6 min is equal to $6.3\times10^{-4}$ mol<br>In the second case n ($MnO_4^-$) remaining at 6 min is less than $6.3\times10^{-4}$ mol. | 0.75 |