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 a volume V of the compound A is heated. At equilibrium, a quantity of 0.3 mol of an ester E of molecular formula $C_5H_{10}O_2$ is obtained.

Given:

- Density of the liquid A is d = 0.78 g. mL^{-1}.
- Molar atomic mass in g.mol^{-1} : M(H) = 1 ; M(O) = 16 and M(C) =12.
- 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- Calculate the volume V of the compound (A) that should be used so that the initial mixture of the acid and the alcohol is equimolar.

2.4- Show that the equilibrium constant of the equilibrium realized previously is equal to 2.25
2.5- Identify the alcohol (A) and name the ester (E).
2.6- The previous study is carried out again but with one change: the ethanoic acid is replaced with ethanoic anhydride.
Calculate the mass of the ester (E) obtained in this case.

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.

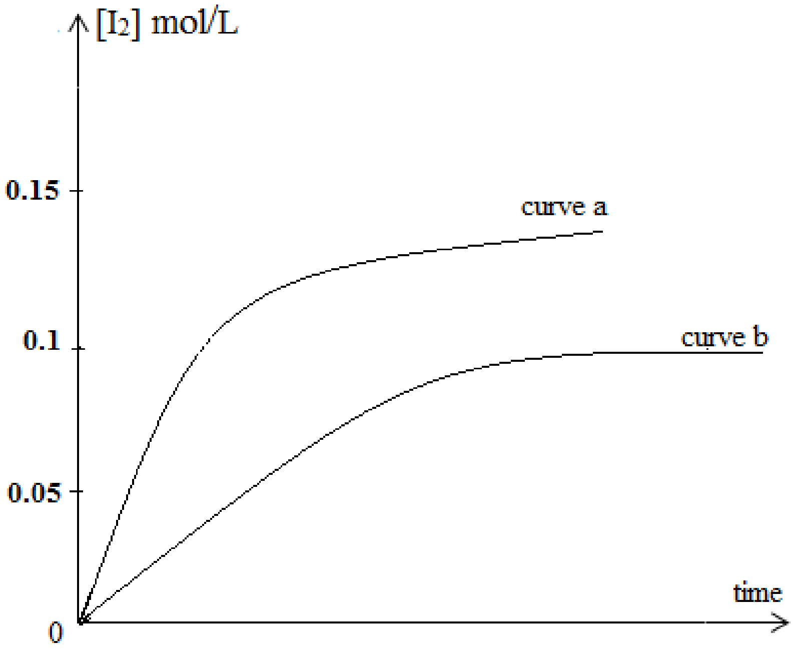
1.1- List the essential materials needed to carry out this preparation.
1.2- Calculate the molar concentration C of this solution.

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 Δt denotes the end time of reaction for each of the reacting mixtures considered in the table below:

Reacting mixture	Temperature of the mixture	Δt
Mixture (1) :a volume V of solution (S)	40°C	Δt_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°C	Δt_2

Verify whether Δt_1 and Δt_2 could be compared.

First exercise (7 points)

Part of the Q	Answer	Mark
1.1	The concentration is: $C_0 = \frac{n_{solute}}{V_{solution} \text{ in L}} = \frac{m_{solute}}{M \times V \times 10^{-3}} = \frac{m_{solution} \times \text{percentage}}{100 \times M \times V \times 10^{-3}} =$ $\frac{d \times V \times \text{percentage}}{M \times V \times 10^{-1}} = \frac{1.47 \times 46 \times 10}{81} = 8.35 \text{mol.L}^{-1}$.	1
1.2	During dilution, the number of moles of the solute is conserved. $F = \frac{C_0}{C} = \frac{V}{V_0} = 200$; so $V_0 = \frac{1000}{200} = 5$ mL. Take using a volumetric pipet of 5 mL and a pipet-filler, 5 mL of the commercial solution, pour them into 1 L volumetric flask containing a certain quantity of distilled water. Complete the volume with distilled water to reach the line mark. Shake well to homogenize the solution.	1
1.3.1	The concentration of the solution (S) is $C_S = \frac{8.35}{200} = 0.041$ mol.L^{-1}. $-\log C_S = -\log 0.041 = 1.38 = pH$. Therefore HBr is a strong acid.	0.75
1.3.2	The equation of the reaction of HBr with water is: $HBr + H_2O \rightarrow H_3O^+ + Br^-$	0.5
2.1	The equation of the titration reaction is : $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	0.5
2.2	At the equivalence point, the chemical species present in the medium, other than water, are NH_4^+ and Br^-. Br^- is spectator ion, while NH_4^+ is an acid that reacts with water to make the medium acidic.	0.5
2.3	At the equivalence point, the number of moles of NH_3 in 10 mL of the ammonia solution is equal to the number of moles of H_3O^+ in Va_E : $Cb \times Vb = Ca \times Va_E$. $Cb = \frac{0.041 \times 12}{10} = 5.0 \times 10^{-2}$ mol.L^{-1}.	0.75
2.4	The volume of ammonia needed to prepare 1 L of the ammonia solution is $V = n \times V_m = 0.05 \times 24 = 1.20$ L.	0.5
3	In order to prepare this buffer solution, H_3O^+ must be the limiting reactant. According to the equation of the reaction (part 2.1): NH_3 + H_3O^+ → NH_4^+ + H_2O Initial state: $Cb \times V_2$; $C_S \times V_1$; 0 ; solvent Final state: $Cb \times V_2 - C_S \times V_1$; 0 ; $C_S \times V_1$; solvent	1.5

	Applying the relation : pH = pKa + log $\frac{[NH_3]}{[NH_4^+]}$=……, therefore $9 = 9.2 + \log\frac{0.05\times50-0.041V_1}{0.041V_1}$ $\log\frac{0.05\times50-0.041V_1}{0.041V_1} = -0.2$ $\frac{0.05\times50-0.041V_1}{0.041V_1} = 0.63$ So V_1 = 36.7 mL	

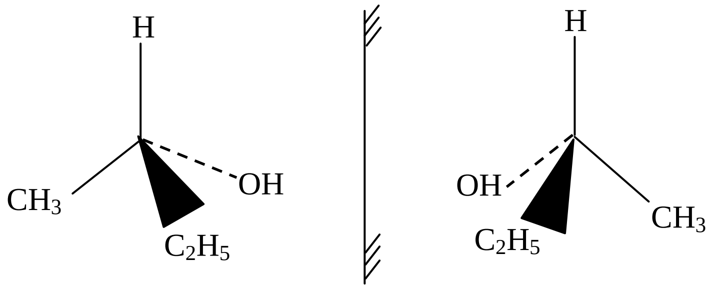
Second exercise (6 points)

Part of the Q	Answer	mark
1.1	(A) plays the role of an acid since its reaction with a metal releases hydrogen gas.	0.5
2.2	From the experiment 2, (A) can be either an alcohol or a carboxylic acid. Therefore the compound B can be a chloroalkane or an acyl chloride.	0.5
2.3	Since (B) contains only carbon, hydrogen and chlorine, therefore B is a chloroalkane and by consequence the compound (A) is a saturated noncyclic chain alcohol of general formula $C_xH_{2x+2}O$.	0.5
2.1	According to the law of the conservation of mass : n(atom of C) in the alcohol = n(atom of C) in the ester - n(atom of C) in the acid = 3. Therefore the molecular formula of (A) is C_3H_8O.	0.75
2.2	The possible condensed structural formulas of the ester (E) are: $CH_3 – COO – CH_2 – CH_2 – CH_3$ and $CH_3 – COO – CH (CH_3)_2$.	0.5
2.3	n (A) initial = $\frac{m(A)initial}{M(A)} = \frac{d(A)\times V}{M(A)}$ = 0.5; so V = $\frac{60\times0.5}{0.78}$ = 38.5 mL.	0.75
2.4	$RCOOH_{(l)}$ + $R'OH_{(l)}$ ⇄ $RCOOR'_{(l)}$ + $H_2O_{(l)}$ Initial state: 0.5 mol, 0.5 mol, -, - Equilibrium state: 0.2 mol, 0.2 mol, 0.3 mol, 0.3 mol K = $\frac{[RCOOH]\times[R'OH]}{[RCOOR']\times[H_2O]} = ... = \frac{0.3\times0.3}{0.2\times0.2} = 2.25$	1
2.5	Since the equilibrium constant K is equal to 2.25, therefore (A) is a secondary alcohol of formula $CH_3 – CHOH – CH_3$; 2-propanol. The name of the ester is 1-methylethyl ethanoate.	0.75
2.6	When ethanoic acid is replaced by ethanoic anhydride, the esterification reaction becomes complete and n (ester) obtained will be equal to0.5 mol. m (ester) obtained = n (ester) x M (ester) = 0.5 x 88 = 44 g.	0.75

Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	The essential materials are: precision balance, spatula, funnel, watch glass and 500 mL volumetric flask.	**1.25**
1.2	Concentration of this solution: $C = \frac{n(solute)introduced}{V(solution)} = \frac{m(solute)introduced}{M(solute)\times V(solution)} = \frac{25}{248\times 0.5}$ =0.20 mol.L^{-1}	**0.75**
2.1	To stop the reaction of formation of iodine, the volume taken is poured into icy water. This choice decreases the temperature as well as the concentration of the reactants that makes the rate of the reaction almost null and the reaction will be stopped.	**0.75**
2.2.1	At equivalence the color of the medium turns from blue to colorless with one drop in excess.	**0.5**
2.2.2	- Limiting reactant: $R_{I^-} = \frac{n(I^-)initial}{2} = \frac{C_1\times V_1}{2} = \frac{0.80\times 0.1}{2} = 0.04$. $R_{S_2O_8^{2-}} = \frac{n(S_2O_8^{2-})initial}{1} = C_2\times V_2 = 0.20\times 0.1 = 0.02$ $R_{S_2O_8^{2-}} < R_{I^-}$; $S_2O_8^{2-}$ is the limiting reactant. $n(I_2)$ formed at the end of the reaction = $n(S_2O_8^{2-})$ initial = 0.02 mol. and $[I_2]$ at the end = $\frac{0.02}{0.2}$ = 0.1 mol.L^{-1} The curve (a) exceeds the value of 0.1, therefore the curve (b) corresponds to the variation $[I_2] = f(t)$.	**1.5**
3.1	The half-life time of the reaction is the time needed for the quantity of the limiting reactant to lose half of its initial value.	**0.5**
3.2.2	$t_{1/2}$ < 35 min, because the reaction rate decreases with time and consequently the transformation of the 1st half of the quantity of the limiting reactant takes a smaller time than that of the 2nd half.	**0.75**
3.3	Passing from mixture 1 to mixture 2: - The concentrations of the reactants are the same. - The temperature decreases and the rate of the reaction decreases. - Fe^{2+} ions catalyze the mixture 2 and the rate of the reaction increases. Therefore, we cannot compare Δt_1 and Δt_2 because each kinetic factor changes the rate in an opposed direction.	**1**

Second Exercise (6 points) (L.S)

Part of the Q	Answer	Mark
1.1	(A) plays the role of an acid since its reaction with a metal releases hydrogen gas.	**0.5**
1.2	From the experiment 2, (A) can be either an alcohol or a carboxylic acid. Therefore the compound B can be a chloroalkane or an acyl chloride.	**0.5**
1.3	Since (B) contains only carbon, hydrogen and chlorine, therefore B is a chloroalkane and by consequence the compound (A) is a saturated noncyclic chain alcohol of general formula $C_xH_{2x+2}O$.	**0.5**
2.1	According to the law of the conservation of mass : n(atom of C) in the alcohol = n(atom of C) in the ester - n(atom of C) in the acid = 4. Therefore the molecular formula of (A) is $C_4 H_{10}O$.	**0.75**
2.2	The possible condensed structural formulas of the ester (E) are: $CH_3 – COO – CH_2 – CH_2 – CH_2 – CH_3$; $CH_3 – COO –CH_2 – CH (CH_3)_2$. $CH_3 – COO - C(CH_3)_3$; $CH_3 – COO –CH(CH_3)– CH_2 –CH_3$.	**1**
2.3	$RCOOH_{(l)} + R'OH_{(l)} \rightleftarrows RCOOR'_{(l)} + H_2O_{(l)}$ Initial state: 0.5 mol, 0.5 mol, -, - Equilibrium state: 0.2 mol, 0.2 mol, 0.3 mol, 0.3 mol K = $\frac{[RCOOH]\times[R'OH]}{[RCOOR']\times[H_2O]} = ... = \frac{0.3\times0.3}{0.2\times0.2} = 2.25$	**1**
2.4	Since the equilibrium constant K is equal to 2.25, therefore (A) is a secondary alcohol of formula $CH_3 – CH(OH) – CH_2 –CH_3$. This is 2- butanol. The name of the ester is 1-methylpropyl ethanoate.	**1**
2.5	The two enantiomers are: 	**0.75**