مسابقة في الكيمياء	الاسم:
المدة: ســـاعتان	الرقم:

This Exam Includes **Three Exercises.** It Is Inscribed On three Pages Numbered from **1** to **3**
Use Of A Non-programmable Calculator Is Allowed.

Answer the Following Three Exercises:

First Exercise (7 points)
Kinetic of Mild Oxidation of an Alcohol

The purpose of this exercise is to study the kinetic of the mild oxidation reaction of a secondary alcohol (A), C_3H_8O, by a potassium permanganate solution acidified with a sulphuric acid solution, H_2SO_4, according to the following equation of the slow reaction:

$$2\ MnO_4^- + 5\ C_3H_8O + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ C_3H_6O + 8\ H_2O$$

I- Identification of the Alcohol (A) and the Oxidation Derivative (B)

1- Write the condensed structural formula of the alcohol (A) and give its systematic name.
2- Write the condensed structural formula of the oxidation product (B) and give its systematic name.
3- Record what would be observed if a sample of compound (B) is treated with :
 a) Schiff's reagent
 b) 2,4- dinitrophenylhydrazine (DN PH) .

II- Preparation of the Initial Solution

It is required to prepare a volume V = 100 mL of a solution (S) by mixing:
- V_1 = 50 mL of a potassium permanganate solution of concentration C_1 = 0.2 $mol.L^{-1}$;
- V_2 = 15 mL of a sulphuric acid solution of concentration C_2 = 6 $mol.L^{-1}$;
- V_3 = 1 mL of the alcohol (A) of density d = 0.8 $g.mL^{-1}$ and of molar mass M_A = 60 $g.mol^{-1}$;
- Enough distilled water to reach the volume 100 mL.

1- Show that, at instant t = 0, we have the following concentrations in (S) :
 $[MnO_4^-]_0 = 0.10\ mol.L^{-1}$; $[H^+]_0 = 1.8\ mol.L^{-1}$ and $[C_3H_8O]_0 = 0.133\ mol.L^{-1}$.
2- Determine the limiting reactant.

III- Kinetic study

At different instants t, the concentrations of C_3H_6O are determined, by an appropriate method. The experimental results are given in the following table:

t (min)	0	1	2	3	4	6
$[C_3H_6O]$ (10^{-3} $mol.L^{-1}$)	0	35	55	68	78	92

1- Plot, on a graph paper, the curve $[C_3H_6O]$ = f(t). Take the following scale :
 abscissa : 1 cm = 1 min ; ordinate: 1 cm = 10×10^{-3} $mol.L^{-1}$.
2- Determine, graphically, the half-life of the reaction.
3- Determine the rate formation of C_3H_6O at t = 3 min.

Second Exercise (7 points)
Household product:˝Destop˝

˝Destop˝ is a household product used as a drain cleaner. It is a commercial concentrated solution of sodium hydroxide. The purpose of this exercise is to titrate the sodium hydroxide in ˝Destop˝ with a hydrochloric acid solution.

Given:

- This titration is performed at 25 ºC.
- Molar mass of sodium hydroxide : M(NaOH) = 40 $g.mol^{-1}$.

I- Procedure of Titration

These steps are followed in the laboratory:

- 500 mL of a solution (S) are prepared by diluting a sample of ˝volume (V_0) of Destop˝ 100 times diluted.
- A volume V_b = 20 mL of solution (S) is poured into a beaker and enough distilled water is then added to immerse the combined electrode of the pH-meter.
- A pH-meter is used to titrate solution (S) with a hydrochloric acid solution of concentration $C_a = 7.2x10^{-2}$ $mol.L^{-1}$.
- The volume of the acid solution needed to reach the equivalence point, which is determined graphically, is V_{aE} = 16.8 mL.

1- Determine the volume V_0 that should be taken from ˝Destop˝ solution to prepare the solution (S).

2- Choose, from the **list** below, the glassware :

a) used to measure the volume V_b ;

b) from which the acid is added into the beaker.

The list

- 50 ; 100 and 500 mL volumetric flasks ;
- 5 ; 10 and 20 mL volumetric pipets ;
- 25 mL buret ;
- 100 ; 250 and 500 mL beakers.

3- The titration of the above ˝Destop˝ is carried out after dilution. Give two reasons that justify this dilution.

II- Make Use of Results

1- Write the equation of the titration reaction.

2- Determine the concentration of sodium hydroxide in solution (S).

3- Deduce the percentage by mass of sodium hydroxide in the ˝Destop˝ solution, knowing that the density of ˝Destop˝ solution is d = 1.22 $g.mL^{-1}$.

4- Justify if the addition of distilled water into the beaker to immerse the combined electrode of the pH-meter affects each of the following:

a) The initial value of pH of solution (S);

b) The value of pH at equivalence;

c) The volume V_{aE}.

Third Exercise (6 points)
Aspirin

Given :

- pK_a (acetylsalicylic acid/acetylsalicylate) = 3.5
- Molar mass of salicylic acid: M_1 = 138 $g.mol^{-1}$.
- Molar mass of acetylsalicylic acid: M_2 = 180 $g.mol^{-1}$.
- pH of the gastric fluid (stomach) is 1.2 and that of the small intestine fluid is 5.5.

We read on a box of common Aspirin the following information:

*** Composition**

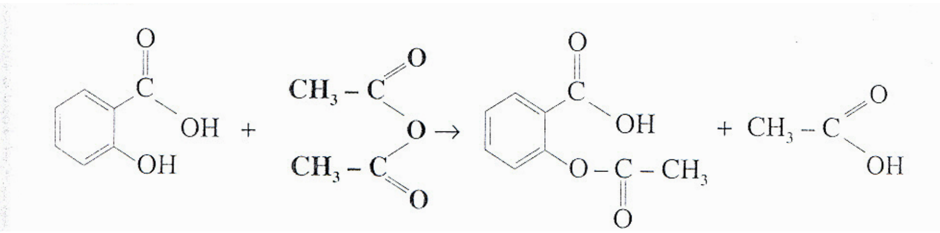
- Acetylsalicylic acid: 0.3 g per tablet.
- Excipient: starch, silica gel.
- ….

*** Warning:**

- Solid aspirin irritates the gastric membrane.
- ….

I- Hemisynthesis Of Aspirin

The hemisynthesis of aspirin is obtained by the acetylation of salicylic acid according the following equation:



Salicylic acid (**X**) *Acetylsalicylic acid* **(Y)**

1- Give the name of each of the two compounds (**X**) and (**Y**).
2- Recopy on the answer sheet the formula of acetylsalicylic acid. Circle the two functional groups containing oxygen and name them.
3- Determine the number of moles of salicylic acid needed to obtain 100 tablets of common aspirin knowing that the yield of hemisynthesis of aspirin is 90 %.

II- Solubility of Aspirin

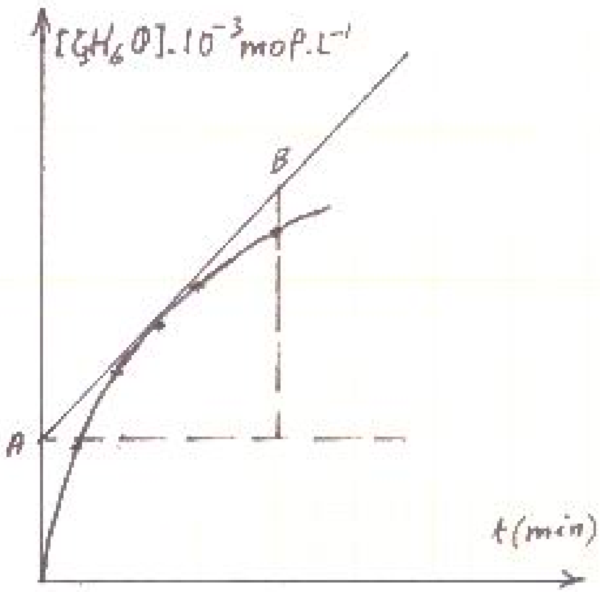
Three small beakers (labeled **a, b, c**), contain respectively : 50 mL of 0.1 $mol.L^{-1}$ hydrochloric acid solution; 50 mL of 0.1 $mol.L^{-1}$ sodium hydroxide solution and 50 mL distilled water.
A tablet of common aspirin is carefully crushed and introduced into each beaker. The content in each beaker is shaken with a magnetic stirrer.
The observation of the three beakers shows that aspirin is very soluble in beaker **b**, slightly soluble in beaker **c,** almost insoluble in beaker **a**. The equation of the reaction of acetylsalicylic acid, represented as HA, with water is :

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

1- Based on the above observations, deduce how the solubility of aspirin changes with the pH of the medium.
2- Using a predominance domain diagram of the species HA and A^- of aspirin, specify the species that predominates in each of the solutions present in the beakers **a** and **b**. Deduce the species of aspirin that predominates in the stomach and in the small intestine.
3- A tablet of aspirin should be crushed and taken with a large amount of water. Justify this fact.

First Exercise (7 points)

Kinetic of the Mild Oxidation of an Alcohol

Expected Answer	Mark	Comments
I-		
1- Since (A) is a secondary alcohol, the condensed structural formula of (A) is then: $CH_3 - CHOH - CH_3$, its name is 2-propanol.	0.5	0.25 formula, 0.25 name
2- The mild oxidation of the secondary alcohol, (A), leads to a ketone of condensed structural formula is: $CH_3 - CO - CH_3$ which is propanone.	0.5	
3- a) No reaction with schiff's reagent since it is a ketone. (nothing is observed. b) The reactant that permits to identify a ketone is the DNPH that gives a yellowish (orange) precipitate.	2x0.5	
II-		
1- The concentration of a species is given by: $C_{mol.L^{-1}} = \frac{n(mol)}{V(solution\,L)}$. It is a dilution, where the number of moles of solute dose not change, we will have then:	0.25	
$[MnO_4^-]_0 = \frac{C_1V_1}{V} = \frac{0.2x50x10^{-3}}{100x10^{-3}} = 0.1\ mol.L^{-1}$.	0.25	
$[H^+]_0 = \frac{2x6x15x10^{-3}}{100x10^{-3}} = 1.8\ mol.L^{-1}$.	0.5	
$[C_3H_8O] = \frac{n(C_3H_8O)}{V} = \frac{d.V_3}{M.V} = \frac{0.8x1}{60x100x10^{-3}} = 0.133\ mol.L^{-1}$.	0.5	
2- According to the stoichiometric coefficients : $R\ (C_3H_8O) = \frac{0.13.V}{5} < R\ (MnO_4^-) = \frac{0.1.V}{2} < R\ (H_3O^+) = \frac{1.8.V}{6}$. Alcohol (A) is then the limiting reactant.	0.5	
III- 1-  0 1 2 3 4 5 6	1	
2- The half life of a reaction is the time needed for half the initial amount of the limiting reactant to disappear. The concentration of	1	

C_3H_6O formed becomes $\frac{0.133}{2}$ = 0.066 mol.L^{-1}. at $t_{1/2}$ = 3.7 min (see the graph). 3- The rate of formation of C_3H_6O at t = 3 min is equal to r = $\frac{d[C_3H_6O]}{dt}$ which is equal to the slope of the tangent, at point of abscissa = 3, on the curve [C_3H_6O] = f(t). Two points are chosen, on this tangent: A (0 – 38×10^{-3}) and B(6 – 104×10^{-3}), then : $r_3 = \frac{(104-38)\times10^{-3}}{6-0}$ = 11×10^{-3} mol.L^{-1}.min^{-1}.	1	

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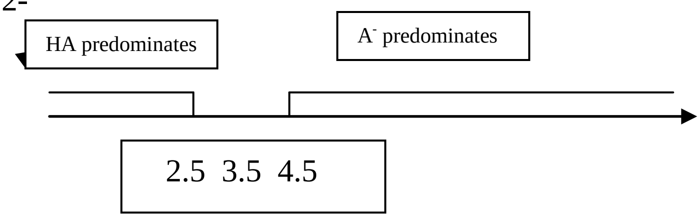
Second Exercise (7 points)
Household Product ″Destop″

Expected Answer	Mark	Comment
I- 1- The dilution factor = 100 = $\frac{V}{V_0}$, where $V_0 = \frac{500}{100}$ = 5 mL.	1	
2- a)A volumetric pipet of 20 mL is used to measure the volume V_b. b)A buret is used to pour the hydrochloric acid solution into the beaker.	0.5 0.5	
3- *Performing the titration by using the Destop without dilution needs a large amount of acid to reach equivalent point, so we need to use the buret several times which increases the errors *The use of a pH-meter is restricted to diluted solution, if we use the Destop without dilution, the pH reading will not be accurate.	2x0.25	- Safety factor
II- 1- The equation of the titration reaction is: $H_3O^+ + HO^- \rightarrow 2\ H_2O$	0.5	
2- At equivalence point, we have: n (HO^-) $_{\text{in 20 mL of (S)}}$ = n (H_3O^+) $_{\text{in 16.8 mL the acid solution}}$. in a solution : n (solute) = CxV. We obtain: $C_{(S)} = \frac{7.2x10^{-2}x16.8x10^{-3}}{20x10^{-3}}$ ≈ 6.05x10^{-2} mol.L^{-1}.	1	
3- Since the solution (S) is obtained by diluting the Destop solution100 times .The value of C is = 6.05 mol.L^{-1}. The mass of NaOH in one liter of the Destop solution is then m = 6.05x40 = 242 g. The mass of one liter of Destop is: 1.22x1000 = 1220 g. The mass percentage of sodium hydroxide in the Destop solution is then: $\frac{242x100}{1220}$ = 19.8 %.	3x0.5	
4- a) The dilution of the basic solution (S) decreases the concentration of HO^-, and hence the pH value. So the initial pH decreases.	0.5	
b) The pH at equivalence point depends on the strength of the acid and that of base used which are both strong so pH at equivalence is equal to 7.	0.5	
c) The addition of distilled water into the beaker doesn't affect the number of moles of solute. So V_{aE} is not affected.	0.5	

Third Exercise (6 points)
The Aspirin

Expected Answer	Mark	Comment
I-		
1- (X) is ethanoic anhydride. (Y) is ethanoic acid.	0.5	Anhydride :0.25 ; acid : 0.25
2- – COOH: carboxylic acid group; - COO…: ester.	4x0.25	
3- The number of moles $n\text{ (salicylic acid)} = \frac{100}{90}\ n\text{ (acetylsalicylic acid)}$ $n\text{ (salicylic acid)} = 100 \times 0.3 \times \frac{1}{180} \times \frac{100}{90} = 0.185\text{ mol.}$	1	
II-		
1- pH_A is strongly acidic < pH_C = 7 (distilled water) < pH_b which is strongly basic. We conclude that the solubility of aspirin increases when pH increases.	1	
2- 	0.5	
We have: pH_a < 2.5, then HA predominates in the beaker **a**. pH_c > 4.5, then A^- predominates in the beaker **b**.	1	
In the gastric fluid, the pH = 1.2 < 2.5, HA predominates. In the intestinal fluid, the pH = 5.5 > 4.5, A^- predominates.	0.5	
3- Since the solid aspirin irritates the gastric membrane, we have to avoid the accumulation of solid agglomerates on this membrane. For this reason an aspirin tablet should be crushed and taken with a large amount of water to disperse and distribute the solid particle in the stomach we should dilute the gastric environment in order to increase the dissolved quantity of aspirin.	0.5	