مسابقة في مادة الكيمياء
المدة ساعتان

الاسم:
الرقم:

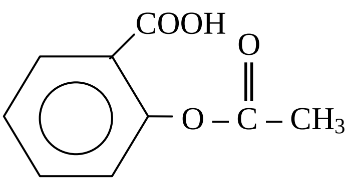
This Exam Includes **Three Exercises**. It Is Inscribed on Four Pages Numbered from **1** to **4**.
The Use of A Non-programmable Calculator Is Allowed

Answer the three following Exercises:

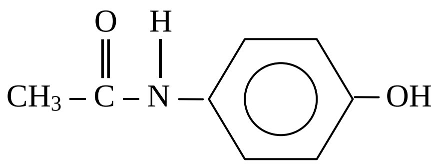
First Exercise (6 points)
Benorilate

"Benorilate" which is the ester of acetylsalicylic acid and paracetamol, is the active ingredient of a medicinal drug named SALIPRAN.

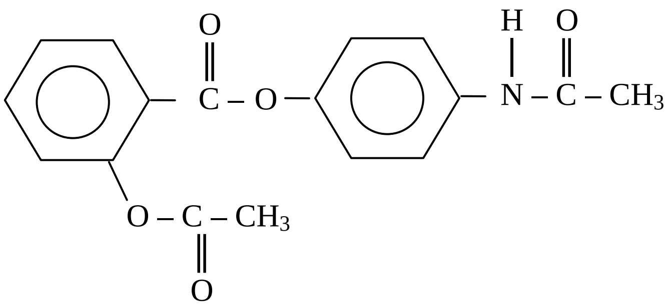
Given:



Acetylsalicylic acid (compound A)



Paracetamol (compound P)



Benorilate (compound B)

1- Paracetamol

Paracetamol is prepared by a reaction of ethanoic anhydride with para (aminophenol).

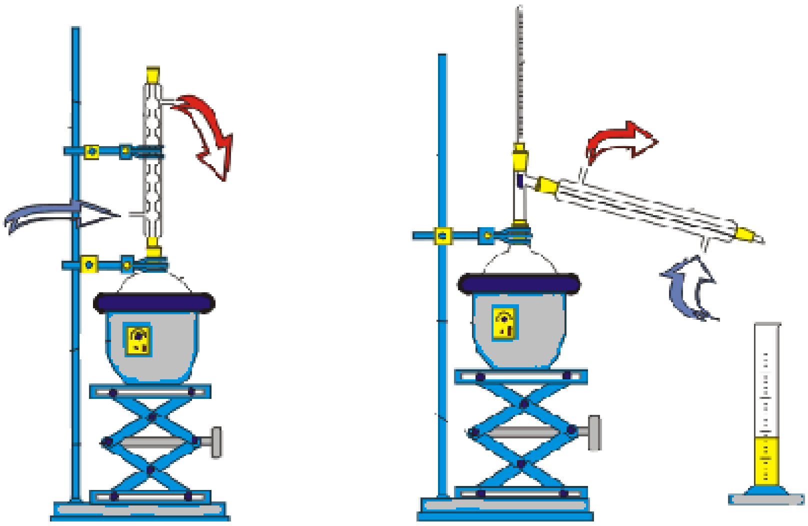
1.1- Write the equation of this reaction.

1.2- Copy, on the answer sheet, the formula of paracetamol, circle its two functional groups and give their names.

2- Acetylsalicylic Acid

To prepare acetylsalicylic acid or aspirin, a mixture of ethanoic anhydride and salicylic acid is subject to reflux heating, in the presence of few drops of concentrated sulfuric acid.

2.1- Choose, by justifying, among the two setups represented below, the convenient one to carry out this preparation.



Setup (a) Setup (b)

2.2- Write the equation of the reaction of synthesis of aspirin.
2.3- Specify the reason for which ethanoic anhydride is used instead of ethanoic acid in this preparation.
2.4- Indicate the role of sulfuric acid in this reaction.

3- <u>Benorilate</u>

<u>Given</u>: Molar mass in $g.mol^{-1}$:
M(aspirin) = 180; M(paracetamol) = 151; M(Benorilate) = 313.

The leaflet of the medicinal drug SALIPRAN presents, among others, the following indications:

- Composition by bag: *Benorilate* 2 g
- Mode of administration: *the content of each bag should be diluted in a cup of water and swallowed immediately.*

3.1- Benorilate (B) is prepared from aspirin (A) and paracetamol (P) according to the reaction of the following equation:

$$A + P \rightleftharpoons B + D$$

3.1.1- Name this reaction.
3.1.2- Identify compound D.

3.2- The content of a bag of Benorilate is prepared from 1150 mg of aspirin and 964 mg of paracetamol. Verify the indication on the leaflet concerning the composition of the bag, knowing that the reaction is made complete.

3.3- Specify the reason for which it is necessary "to swallow immediately the content of the bag after dilution in water".

Second Exercise (7 points)
Oxidation of Iodide Ions

Iodide ions I^- are oxidized by peroxydisulfate ions $S_2O_8^{2-}$ in a slow and complete reaction according to the following equation:

$$2\,I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow I_{2(aq)} + 2\,SO_4^{2-}{}_{(aq)}$$

At instant t = 0, a mixture S is prepared by mixing a volume V_1 = 10 mL of potassium iodide solution of concentration C_1 = 0.50 mol.L $^{-1}$ with a volume V_2 = 10 mL of sodium peroxydisulfate solution of concentration C_2 = 5.0x10 $^{-3}$ mol.L $^{-1}$.

1- Study of the Reactional Mixture

1.1- Determine the limiting reactant in mixture S.

1.2- Draw a table representing the number of moles of the components of S in its initial and final state.

2- Kinetics of this Reaction

The kinetic of the formation of iodine in mixture (S), by an appropriate physical method, permits to measure the quantity of I_2 formed, n (I_2), versus time t according to the following table:

n(I_2)(10^{-6} mol)	4.80	8.00	13.6	18.6	22.8	30.0	34.8	38.6	43.6	….	46.5
t (min)	1	2	4	6	8	12	16	20	30	…..	60

2.1-Plot the curve representing the variation of n (I_2) versus time in the interval:
0 – 30 min.
Take the following scale:
abscissa: 1 çm for 2 min and ordinate: 1çm for 4x10 $^{-6}$ mol.

2.2- Determine:

2.2.1- The rate of this reaction at t = 16 min.

2.2.2- The half-life of this reaction $t_{1/2}$.

3- Titration of Iodine Formed After 60 Minutes

It is required to verify, by titration, the number of moles of I_2 given in the above table of part **2** at time t = 60 min. For that, the following procedure is carried out:

- A volume V = 5.0 mL of the reactional mixture (S) is introduced into a beaker containing ice-water at time t = 60 min.
- The iodine present in volume V is titrated with a sodium thiosulfate solution ($2Na^+ + S_2O_3^{2-}$) of concentration C´= 2.0x10 $^{-3}$ mol.L $^{-1}$, in the presence of few drops of starch solution.

The equation of this reaction is:

$$I_{2(aq)} + 2\,S_2O_3^{2-}{}_{(aq)} \rightarrow 2\,I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

The volume of the thiosulfate solution added to reach equivalence is V'_E =11.6 mL.

3.1- Indicate the kinetic factors involved when volume V is introduced into the ice-water beaker. Deduce the purpose of this operation.

3.2- Note the variation of color observed in the beaker at equivalence.

3.3- Verify the value of n(I_2) which is given in the table of part **2** at time t = 60 min,.

Third Exercise (7 points)
Javelle water

Javelle water is an aqueous solution of sodium chloride and sodium hypochlorite. Hypochlorite ion, ClO^-(aq), is the active constituent of Javelle water and the conjugate base of hypochlorous acid HClO(aq).

Given:

- This study is performed at 25°C.
- $pK_a(CO_2,H_2O/HCO_3^-)$ = 6.4.
- $K_w = 1.0 \times 10^{-14}$.

- Molar mass: $M(Cl) = 35.5\ g.mol^{-1}$.
- Chlorine is a toxic gas.

1 - Acid-base Properties of Javelle Water

1.1- Write the equation of the acid-base reaction between hypochlorite ion and water.

1.2- Determine the value of pKa of the conjugate acid/base pair ($HClO/ClO^-$), knowing that the degree of transformation of ClO^- is 0.50 when the pH of the solution is equal to 7.3.

1.3- Carbon dioxide of air reacts with hypochlorite ion according to the following equation:

$$ClO^- + CO_2,H_2O \rightleftharpoons HClO + HCO_3^-$$

1.3.1- Determine the equilibrium constant K of this reaction.

1.3.2- Explain why Javelle water is stored in well closed bottles.

2 – Javelle Water: Danger!

The pH of a sample of Javelle water is made 2.0. At this value of pH, the following reaction takes place:

$$HClO_{(aq)} + Cl^-_{(aq)} + H_3O^+_{(aq)} \rightarrow Cl_{2\,(g)} + 2\ H_2O.$$

2.1- Identify the predominant specie of the pair $HClO/ClO^-$ at pH = 2.

2.2- A detergent bottle containing hydrochloric acid is labeled: "do not mix with Javelle water". Justify this affirmation.

3 - Treatment of a Swimming Water Pool by Javelle Water

In most swimming pools, Javelle water is added to kill harmful bacteria by hypochlorite ions.

3.1- To make this process efficient, it is necessary to maintain the pH of water between 7.0 and 7.6.

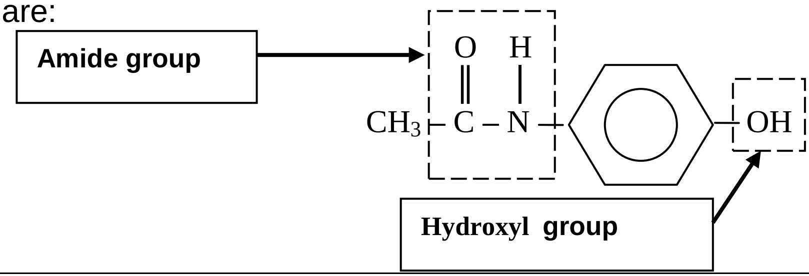
Show that none of the two species ClO^- and HClO is predominant in the water of swimming pools at the above recommended pH range.

3.2- To avoid dangerous problems in swimming pools, the mass concentration of the element chlorine (in the two forms HClO and ClO^-) should be between 1 and 2 $mg.L^{-1}$.

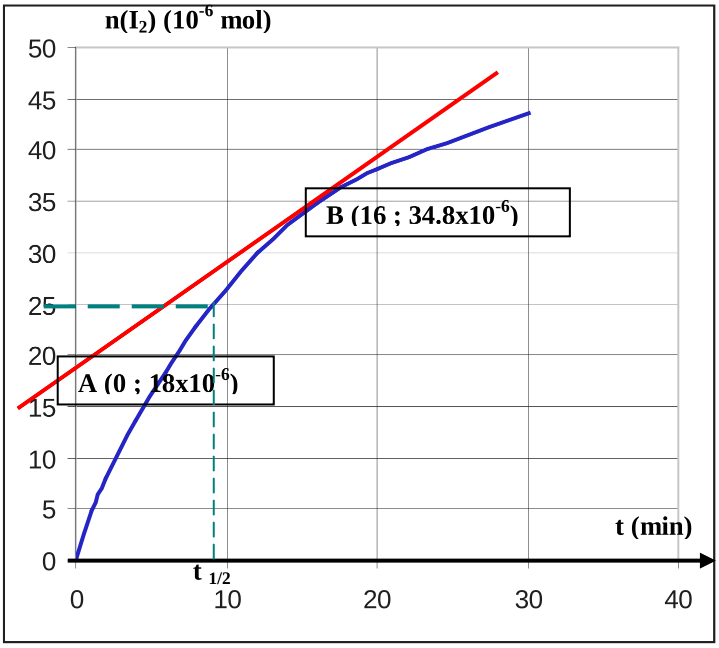
In the water of a swimming pool, the concentration of hypochlorite ions ClO^- is $2 \times 10^{-5}\ mol.L^{-1}$.

Verify that the water of this swimming pool has an acceptable concentration of the element chlorine knowing that the pH of this water is 7.3.

First Exercise(6 points)

Part	Answer	Mark
1	**Paracetamol**	
1.1	The equation of this reaction is: $CH_3 – CO – O – CO – CH_3 + HO – C_6H_4 – NH_2 \rightarrow$ $HO – C_6H_4 – NH – CO – CH_3 + CH_3 – COOH$	**0.75**
1.2	The two groups are: : 	**1**
2	**Acetylsalicylic Acid**	
2.1	The setup (a) is convenient to perform the reflux heating. This setup makes it possible to heat the reactional system without losing any component of this system. While in the setup (b) there is separation of the components of the system by heating.	**0.5**
2.2	The equation of this reaction is: $CH_3 – CO – O – CO – CH_3 + HO – C_6H_4 – COOH \rightarrow$ $CH_3 – CO – O – C_6H_4 – COOH + CH_3 – COOH$	**0.75**
2.3	The anhydride is used instead of the acid in order to make the reaction complete.	**0.5**
2.4	Sulfuric acid is a catalyst in this reaction.	**0.25**
3	**Benorilate**	
3.1.1	It is an esterification reaction.	**0.25**
3.1.2	(D) is obtained by reaction of the group – OH of paracetamol and the hydrogen of the carboxyl group of aspirin. Its formula is then H_2O, its name is water.	**0.5**
3.2	The number of moles is given by $n = \frac{m}{M}$, we have: $n(\text{aspirin})_{\text{initial}} = \frac{1.150}{180} = 6.38 \times 10^{-3}$ mol ; $n(\text{paracetamol})_{\text{initial}} = \frac{0.964}{151}$.= 6.38×10^{-3} mol. Reaction being complete, $n(\text{Benorilate})_{\text{obtained}} = 6.38 \times 10^{-3}$ mol whose mass is $6.38 \times 10^{-3} \times 313 = 1.99$ g. This value verifies the indication of the leaflet concerning the composition of the bag (2 g).	**1**
3.3	It is necessary "to swallow immediately the contents of the bag after dilution" in order to avoid the reaction of hydrolysis of Benorilate.	**0.5**

Second Exercise (7 points)

Part	Answer	Mark
1	**Study of the Reactional Mixture**	
1.1	Limiting reactant in mixture S: $R_{(I^-)} = \frac{n(I^-)initial}{2} = \frac{C_1.V_1}{2} = \frac{0.5x10x10^{-3}}{2}$ = 2.5x10^{-3} $R_{(S_2O_8^{2-})} = \frac{n(S_2O_8^{2-})initial}{1}$ = C$_2$xV$_2$= 5x10^{-3}x10x10^{-3}=5x10^{-5} < $R_{(I^-)}$. $S_2O_8^{2-}$ is the limiting reactant.	0.75
1.2	The table is as follows: $2I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow I_{2(aq)} + 2SO_4^{2-}{}_{(aq)}$ Initial state (mol): 5.10^{-3} ; 5.10^{-5} ; - ; - Final state (mol): ~5.10^{-3} ; 0 ; 5.10^{-5} ; 10.10^{-5}	0.75
2	**Kinetics of this Reaction**	
2.1	The curve  	1.25
2.2.1	The rate of the reaction is equal at the rate of formation of I_2 at any instant t. This rate is equal to the slope of the tangent to the curve: $n(I_2) = f(t)$ at the point of abscissa t: $v_{t=16\ min} = \frac{(34.8-18)x10^{-6}}{16-0}$ = 1.05x10^{-6} mol.min^{-1}.	1
2.2.2	The half-life of the reaction is the time needed to reach the half for the maximum number of moles of I_2 formed : $n(I_2)_{1/2} = \frac{50x10^{-6}}{2}$ = 25x10^{-6} mol which corresponds to: $t_{1/2}$ = 8.5 min.	0.75
3	**Titration of Iodine Formed after 60 Minutes**	
3.1	The two kinetic factors are: - The concentration of the reactant $S_2O_8^{2-}$ in solution S	0.75

	- temperature. The purpose of this operation is to stop the reaction in volume V.	
3.2	The contents of the beaker changes from intense blue coloring (starch solution $+I_2$) to colorless, at equivalence point.	0.5
3.3	At equivalence point, and according to stoichiometry proportion: $n(I_2)$ in V $= \frac{n(S_2O_3^{2-})added}{2} = \frac{C'.V'_E}{2}$ $n(I_2)$ in V $= \frac{C' \cdot V'_E}{2} = \frac{2x10^{-3} x11.6x10^{-3}}{2}$ $=11.6x10^{-6}$mol Where $n(I_2)$ in the mixture S at 60 min = $n(I_2)$ in $Vx\frac{20}{5}$ = $46.4x10^{-6}$mol. It is almost the same value given in part **2**.	1.25

Third Exercise (7 points)

Part	Answer	Mark
1	**<u>Acid-base Properties of Javelle Water</u>**	
1.1	The equation of this reaction: $ClO^- + H_2O \rightleftharpoons HClO + HO^-$	**0.5**
1.2	pH = pKa + log $\frac{[ClO-]}{[HClO]}$ for α = 0.5 half of the amount of ClO^- is transformed to HClO. So $[ClO^-] = [HClO]$ and log $\frac{[ClO-]}{[HClO]}$ = 0 then pH = pKa_1 = 7.3.	**1.25**
1.3.1	$K = = \frac{[HClO]x[HCO_3^-]}{[ClO^-]x[CO_{2,}H_2O]} = 10^{(pK_{A1} - pK_{A2})}$; $K = 10^{(7,3-6,4)} = 10^{0,9} = 7,9$	**1**
1.3.2	It is stored in well closed bottles to avoid the reaction between ClO^- and CO_2 of air . This diminishes the concentration of the active constituent of Javelle water.	**0.75**
2	**<u>Javelle Water: Danger!</u>**	
2.1	At pH = 2,0 ; the predominant specie is hypochlorous acid because the pH of the solution is less than $pK_a - 1$.	**0.75**
2.2	In the presence of an acidic medium, the reaction of hypochlorous acid with H_3O^+ ions produces chlorine gas which is very toxic.	**0.75**
3	**<u>Treatment of a Swimming Water Pool by Javelle Water</u>**	
3.1	Since the pH of the swimming water pool is between $pK_a - 1$ and $pK_a + 1$, none of the species is predominant.	**0.75**
3.2	At pH = 7.3 ; pH = pKa => $[ClO^-] = [HClO]$ then $[HClO] = [ClO^-] = 2x10^{-5}$ $mol.L^{-1}$ In1L of solution: Concentration C of Chlorine= $[HClO] + [ClO^-] = 4x10^{-5}$ $mol.L^{-1}$ $Cg.L^{-1} = Cmol.L^{-1}$ x $M_{Cl} = 4x10^{-5}x\ 35.5 = 1.42x10^{-3}g.L^{-1} = 1.42\ mg.L^{-1}$.	**1,25**

	C_{Cl} is between 1mg.L^{-1} and 2mg.L^{-1}. Then it is acceptable.	