General Sciences Sample
First Exercise
Propanoic Acid Solution

The aim of this exercise is to study the acid character of propanoic acid solution and to prepare a buffer solution.

Given:

- Propanoic acid, C_2H_5COOH, dissociates partially in water.
- pK_a (C_2H_5COOH / $C_2H_5COO^-$) = 4.75.

I- Reaction of Propanoic Acid with Water

1. Write the equation of the the reaction of propanoic acid with water.

2. A student affirms that: *“The only chemical species (whatever the concentration is) in the aqueous solution of propanoic acid are: H_2O, C_2H_5COOH, $C_2H_5COO^-$ and H_3O^+”*. Justify whether this affirmation is correct.

3. The species H_3O^+ and $C_2H_5COO^-$ forms a conjugate acid / base pair. Is this possible? Justify.

II- Effect of Dilution on the pH Measurements

Consider an aqueous solution **S_1** of propanoic acid of concentration $C_1 = 10^{-1}$ mol.L^{-1}. We transfer a volume V_1 of **S_1** to prepare a volume V_2 = 100 mL of an aqueous solution **S_2** of propanoic acid of concentration $C_2 = 10^{-3}$ mol.L^{-1}.

The pH values of **S_1** and **S_2** are designated by pH_1 and pH_2 respectively.

1. Determine the volume V_1.

2. Justify whether each of the following propositions is true or false:

a) $pH_2 > pH_1$ b) $pH_1 = - \log C_1$ c) $pH_2 = pH_1 + 2$ d) $pH_2 < 7$ at 25°C.

III- Reaction between Propanoic Acid and Sodium Hydroxide Solution

The reaction between an aqueous solution of propanoic acid and an aqueous solution of sodium hydroxide can be used for titration.

1. List the necessary conditions for a reaction to be a titration reaction.

2. Write the equation of the reaction occurs between the two solutions.

3. A volume V of sodium hydroxide solution of concentration $C_b = 0.5\times10^{-3}$ mol.L^{-1} is added to a volume V’ = 25 mL of solution **S_2** so that the reactants are in stoichiometric proportions. The mixture obtained is designated by **M.**

a) Determine the volume V.

b) Justify whether the mixture **M** is acidic, basic or neutral.

4. To the mixture **M**, we add a volume V’’= 25 mL of **S_2** to obtain a mixture **N.** Calculate the pH of **N** and deduce the nature of this solution.

5. It is desired to prepare a buffer solution of pH = 5.0. Determine the volume of sodium propanoate solution of 10^{-1}mol.L^{-1} that should be added to 100 mL of the propanoic acid solution $\mathbf{S_1}$ in order to prepare this buffer solution.

Solution:

I-1)

$$C_2H_5COOH + H_2O \rightleftharpoons C_2H_5COO^- + H_3O^+$$

I-2)

The affirmation is false since there is also OH^- comes from the autoionization (autopyrolysis) of water: $2\ H_2O \rightleftharpoons OH^- + H_3O^+$

I-3)

This is not possible because when $C_2H_5COO^-$ accepts a proton it becomes C_2H_5COOH, so C_2H_5COOH is the conjugate acid and they form a pair.

II-1)

Case of dilution: $n_{S1} = n_{S2}$ so $V = (100\times10^{-3}) \div 10^{-1} = 1$ mL.

Fold $F = C_1 / C_2 = 100$.

II-2-a)

S_1 is more concentrated than S_2, so $C_1 > C_2$ and consequently $[H_3O^+]_{S1} > [H_3O^+]_{S2}$

But pH is inversely proportional to $[H_3O^+]$ then $pH_1 < pH_2$

Thus the statement is true.

II-2-b)

Propanoic acid is a weak acid, so $C_{acid} \neq [H_3O^+]$ then $C_1 \neq [H_3O^+]_{S1}$.

But $pH_1 = -\log [H_3O^+]_1$ then $\log C_1 \neq pH_1$.

Thus the statement is false.

II-2-c)

F = 100; for strong acids, upon dilution by 100 folds the pH increases by 2 units. If this acid were strong then $pH_2 = pH_1 + 2$. But this is a weak acid and consequently this proposition is false.

II-2-d)

For acidic solutions, pH is always less than 7 at 25°C. Thus the statement is true.

III-1)

The conditions are: complete, rapid, spontaneous and unique.

III-2)

The reaction is: $C_2H_5COOH + OH^- \rightarrow C_2H_5COO^- + H_2O$

This reaction is considered to be complete since it is used in titration and consequently $pK_{a2} - pK_{a1} = 14 - 4.87 = 9.13 > 4$.

III-3-a

Based on the above reaction: $n(C_2H_5COOH)_{reacted} = n(OH^-)_{reacted}$

But $n(NaOH) = n(OH^-)$

Then $C_2 V' = C V$ so $V = (1\times10^{-3}\times25) \div 0.5 \times 10^{-1} = 50$ mL.

III-3-b)

The main species at the equivalence point (when all C_2H_5COOH and OH^- have reacted), other than water, are Na^+ and $C_2H_5COO^-$. Na^+ is a spectator ion while $C_2H_5COO^-$ is a base that reacts with water to make base solution at equivalence.

$$C_2H_5COO^- + H_2O \rightleftharpoons C_2H_5COOH + OH^-$$

III-4)

The main species present: H_2O, $C_2H_5COOH_{(added)}$ and $C_2H_5COO^-$ (produced from mixture **M**).

By mole ratio of the reaction in (**III-2)** we have:

$n(C_2H_5COOH)_{reacted} = n(OH^-)_{reacted} = n(C_2H_5COO^-)_{produced}$.

So $n(C_2H_5COO^-)$ produced from mixture **M** $= 50 \times 10^{-3} \times 0.5 \times10^{-3} = 0.025 \times 10^{-3}$ mol.

$n(C_2H_5COOH)_{added} = C_{S2} \times V'' = 25 \times 10^{-3} \times 10^{-3} = 0.025 \times 10^{-3}$ mol.

$V_{total} = V_N = V_M + V'' = (50 + 25) + 25 = 100$ mL.

Thus $[C_2H_5COO^-]$ in mixture **N** $= (0.025 \times 10^{-3}) / 0.1 = 0.25 \times 10^{-3}$ mol.L^{-1}.

$[C_2H_5COOH]$ in mixture **N** $= (0.025 \times 10^{-3}) / 0.1 = 0.25 \times 10^{-3}$ mol.L^{-1}.

$pH = pK_a + \log([C_2H_5COO^-] / [C_2H_5COOH]) = pK_a = 4.87$.

So we have a buffer solution that contains the acid and its conjugate base.

III-5)

$C_2H_5COONa \rightarrow C_2H_5COO^- + Na^+$

Since we have the acid C_2H_5COOH and its conjugate base $C_2H_5COO^-$ then:

$pH = pK_a + \log([C_2H_5COO^-] / [C_2H_5COOH])$

$5.0 = 4.87 + \log(C_b V_b / C_a V_a)$

$C_a = 0.1$ mol.L^{-1}; $V_a = 100$ mL and $C_b = 0.1$ mol.L^{-1}.

Solve we get $V_b = 135$ mL.

Second Exercise
Study of a Pharmacological Hydrogen Peroxide Solution

A pharmacological hydrogen peroxide solution **(S_0)**, used as an antiseptic and as hairs' colorizing agent, is labeled **30V**. This indication represents the maximum volume of 30 L of oxygen gas (measured under normal conditions where $V_m = 22.4$ L.mol^{-1}) which is liberated from one liter of hydrogen peroxide solution according to the equation of the following *slow* reaction**:** $\mathbf{2\,H_2O_{2\,(aq)} \rightarrow 2\,H_2O_{(l)} + O_{2\,(g)}}$
This exercise aims to verify the indication **30V** by studying the kinetics of the following reaction:

$$\mathbf{2\,I^-_{(aq)} + H_2O_{2\,(aq)} + 2\,H_3O^+_{(aq)} \rightarrow I_{2\,(aq)} + 4\,H_2O_{(l)}}$$

1- <u>Dilution of the Pharmacological Hydrogen Peroxide Solution</u>

The following materials are available:

- Volumetric pipettes: 1, 2 and 10 mL.
- Volumetric flasks: 50, 100 and 250 mL.
- Beakers: 25, 50 and 100 mL.
- Erlenmeyer flasks: 25, 50 and 100 mL.

1.1-List, from the given materials, the glassware needed to prepare from the original solution **(S_0)**, a solution **(S)** that is 100 times diluted.
1.2-Describe the procedure followed to prepare the solution **(S)**.

2- <u>Kinetic Study and Verification of 30 V</u>

To verify the indication **30 V**, the following procedure is carried out:

- Several beakers are prepared such that each one is containing a volume $\mathbf{V_S}$ = 5 mL of solution **(S)** and a volume $\mathbf{V_1}$ = 10 mL of acidified potassium iodide solution (considered in excess).
- The iodine present in each beaker is titrated, at different instants, with a sodium thiosulfate solution of molar concentration $C_R = 1\times10^{-2}$ mol.L^{-1}, in the presence of few drops of starch solution. The equation of this reaction is: $\mathbf{I_{2\,(aq)} + 2\,S_2O_3^{2-}{}_{(aq)} \rightarrow 2\,I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}}$

The experimental results are given in the following table:

t (s)	0	20	60	120	180	240	300	480	600	900	∞
V_{eq} (mL)	0	2.4	7.1	11.7	13.8	15.6	17.4	20.5	21.3	23.0	27.0
$[I_2]$ (mmol.L^{-1})	0	0.8	2.3	3.9	4.6	----	5.8	6.8	7.1	7.6	-----

2.1-Before starting the titration, icy- water is poured into each beaker.
2.1.1- Indicate the two kinetic factors involved in this operation.
2.1.2- Specify the effect of each one of these two factors on the kinetic of the reaction between iodide ions and hydrogen peroxide.
2.2-Prove that the concentration of the iodine formed $\mathbf{[I_2]_t}$, in mol.L^{-1}, and the equivalence volume of thiosulfate $\mathbf{V_{eq}}$, in mL, at instant t, are related by the following relation: $\mathbf{[I_2]_t = 3.33\times10^{-4}\,V_{eq}}$.
2.3-Find the two missing values in the above table.
2.4-Plot, on a graph paper, the curve $[I_2]$ = f (t) in the interval time [0-900]. Take the following scales: *abscissa:* 1 cm for 100 s; ordinate*:* 1 cm for 1×10^{-3} mol.L^{-1}.
2.5-Determine the rate of formation of iodine at t = 300 s.

2.6-Show, based on the kinetic study, that the molar concentration of hydrogen peroxide in solution (**S**) is equal to 0.027 $mol.L^{-1}$.
2.7-Deduce the molar concentration of H_2O_2 in the commercial solution (**S_0**).
2.8-Show that the indication **30V** is almost verified and conclude the % error.

Answer of the 2nd Exercise

1-1)

To prepare the solution **(S)** of concentration C from the solution (**S_0**) of concentration C_0, the dilution factor is equal to: $10 = V / V_0$

V = volume of the volumetric flask and V_0 is the volume of the pipette.

To carry out the most precise preparation, a volumetric pipette of 1 mL and a volumetric flask of 100 mL constitute the most convenient glassware.

1-2)

Using a **volumetric pipette of 1 mL** provided with a pipette filler, take 10 mL of solution S_0; pour them in a **100 mL volumetric flask;** fill this flask, to the line mark, with distilled water; stopper it and shake it several times to homogenize.

2-1-1)

The two kinetic factors involved in this operation are: temperature of the reaction medium and the concentrations of the reactants.

2-1-1)

In this operation, the temperature decreases and the concentrations of the reactants decrease. The rate of the reaction will decrease in such a way that the reaction will be practically blocked

2.2)

At the equivalence of the titration of the formed iodine:

$n(I_2)_{\text{in beaker}} = ½\, n(S_2O_3^{2-})_{\text{added}} = 0.5 \times C_R \times V_{eq}$

Divide by V_{sample} we get $\mathbf{[I_2]_t = 3.33\times10^{-4}\, V_{eq}}$

2.3)

From the table at t = 240 s, V_{eq} = 15.6 mL so $[I_2]_{240} = 5.2 \times 10^{-3}$ $mol.L^{-1}$.

From the table at t = ∞, V_{eq} = 27 mL so $[I_2]_{\infty} = 9 \times 10^{-3}$ $mol.L^{-1}$.

2.5)

The rate of formation of I_2 at t = 300 s is defined by: $r_{(t = 100)} = d[I_2] / dt$. The value of this rate is equal to the slope of the tangent to the given curve at the point of abscissa t = 300 s.

2.6)

Thus $n(I_2)_\infty = [I_2]_\infty \times V_{mixture} = 9\times10^{-3} \times 15 \times 10^{-3} = 1.35\times10^{-4}$ mol.

According to the stoichiometry of the reaction of H_2O_2 with I^-:

$n(I_2)_\infty = n(H_2O_2)_{initial} = 1.35\times10^{-4}$ mol.

$[H_2O_2]$ of solution **(S) =** n / V_S **=** $(1.35 \times 10^{-4}) \div (5 \times 10^{-3}) = 0.027$ mol.L^{-1}.

2.7)

$[H_2O_2]$ of solution **(S_0) =** $100 \times [H_2O_2]$ of solution **(S)** (Dilution factor = 10)

$= 100 \times 0.027 = 2.7$ mol.L^{-1}.

2.8)

According to the stoichiometry of the decomposition reaction of H_2O_2:

$V_{O2} / V_m = ½ \times [H_2O_2]_{S0} \times V_{H2O2}$

$V_{H2O2} = 1$ L; $V_m = 22.4$ L.mol^{-1}; $[H_2O_2]_{S0} = 2.7$ mol.L^{-1}

So $V_{O2} = 30.24$ L or 30.24 V which is very close to the indication 30V

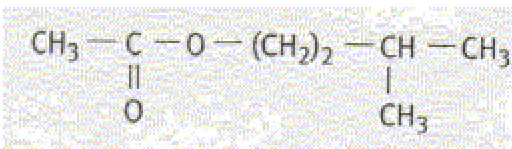
Error = (30 – 30.24) ÷ 30 = 0.008 = 0.8 %

Third Exercise
Synthesis of an Ester

Isoamyl acetate (isopentyl acetate) is an ester that has a strong odor (similar to juicy fruit) which is also described as similar to both banana and pear. It is released by a honey bee's sting apparatus where it serves as a pheromone beacon to attract other bees and provoke them to sting.

Isoamyl acetate can be prepared in the laboratory by the acid catalyzed reaction between isoamyl alcohol and acetic acid.

It is required to prepare the ester **(E)**: isoamyl acetate whose condensed structural formula is shown below:



List of available chemicals:

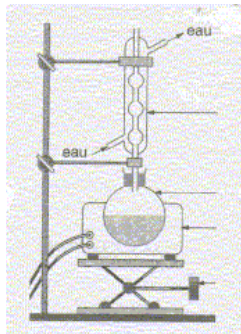
Ethanoic acid, 2-methylbutanoic acid, 2-methyl-1-butanol, 3-methyl-1-butanol, ethanol, dehydrating agent P_4O_{10}, thionyl chloride $SOCl_2$, acidified potassium dichromate solution, Fehling solution, ethanamine $C_2H_5 - NH_2$, Tollens reagent and 2,4 – DNPH.

<u>Given:</u>

- M (isoamyl acetate) =150 $g.mol^{-1}$.
- The yield of the esterification reaction for an equimolar mixture of a primary alcohol and a carboxylic acid is 67%.

I- Esterification Reaction

In order to synthesize the ester **(E)**, 0.10 mol of an acid **(A)**, 0.10 mol of an alcohol **(B)** chosen from the above list and some drops of concentrated sulfuric acid are heated at 60°C in the set up shown below:



1- Give the IUPAC name of the ester **(E)**.
2- Name the above set up and label it. Indicate its role.
3- Write the condensed structural formula of each of **(A)** and **(B)**.
4- Indicate the class of **(B)**. Describe briefly the steps that will be followed to identify this class by using the convenient chemicals from the above list.
5- Write the equation of the reaction between **(A)** and **(B)**. Give its characteristics.

II- <u>Yield of the Reaction</u>

The table below shows the modification of certain experimental conditions of the above reaction:

<table>
<tr><th>Experiment</th><th>Carboxylic acid</th><th>Alcohol</th><th>Sulfuric acid</th><th>Temperature</th></tr>
<tr><td>exp 0</td><td rowspan="4">0.1 mol</td><td rowspan="3">0.1 mol</td><td rowspan="2">0</td><td>60°C</td></tr>
<tr><td>exp 1</td><td>90°C</td></tr>
<tr><td>exp 2</td><td rowspan="2">1 mL</td><td rowspan="2">60°C</td></tr>
<tr><td>exp 3</td><td>0.5 mol</td></tr>
</table>

1- Define the yield of the reaction.
2- Determine the molar composition of the system of experiment 0. Deduce the corresponding mass of isoamyl acetate obtained at equilibrium.
3- Compare experiments 1, 2, 3 with experiment 0. Indicate, for each experiment, the influence of the various parameters on the yield of the reaction.
4- The synthesis of this ester can be carried out by replacing the acetic acid by another organic compound **(X)**. Give its condensed structural formula.
5- Write the equation of the reaction of **(X)** with alcohol **(A)**. Give the characteristics of this reaction.

Solution

The IUPAC name of the ester **(E) is**: **3-methyl-1-butyl ethanoate**

The set up represents the reflux heating; it makes it possible to increase the temperature of the reactional medium. The condensation of the vapors makes it possible to avoid any matter loss. Water circulates from the bottom of the condenser (c) to the top of the condenser (b).

The isoamyl acetate is obtained starting from ethanoic acid (A) and 3-methyl-1-butanol (B). The semi-developed formulas of these compounds are:

CH_3-COOH HO-CH_2-CH_2-CH(CH_3)$_2$

(A) (B)

(B) is a primary alcohol; the oxidation of (B) with acidified potassium dichromate solution gives 3-methyl butanal. The latter compound gives a yellow-orange precipitate with 2,4 – DNPH . 3-methyl butanal gives a brick-red precipitate in the presence of a Fehling solution (in basic medium).

CH_3-COOH + HO-CH_2-CH_2-CH(CH_3)$_2$ ⇌ CH_3-COO-CH_2-CH_2-CH(CH_3)$_2$ +H_2O

The kinetic characteristics: slow, athermic, limited by the hydrolysis of ester.

The initial mixture being equimolar: the reagents are then in stoichiometric proportions.

Yield = 67% = (Actual quantity of ester / theoretical quantity of ester) = x_{final} /x_{max}

Theoretical quantity (mole) of ester = x_{final} = 0.1 mol.

Then x_{max} = 0.01 mol and so mass of isoamyl acetate obtained = 0.067□150 = 10 g.

Experiment 1: the temperature is a kinetic factor; equilibrium is reached more quickly (compared to exp 0) but the molar composition at equilibrium is not modified since the temperature is unchanged

Experiment 2: the sulfuric acid is a catalyst; equilibrium is reached more quickly (compared to experiment 0) but the molar composition at equilibrium is not modified since the temperature is unchanged.

Experiment 3: the sulfuric acid is a catalyst; the quantity of matter of the reagents is a kinetic factor; equilibrium is reached more quickly (compared to experiment 0) and the molar composition at equilibrium is modified; by an excess alcohol, the equilibrium is shifted towards right and so the formation of ester increases.

$[CH_3\text{-}CO]_2O + HO\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)_2 \rightarrow CH_3\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)_2 + CH_3\text{-}COOH$
Characteristics of this reaction: rapid, exothermic and complete thus the yield of the reaction is about 100%.

Life Sciences Sample
First Exercise
Saponfication in Hard Water

Given:

- The formula of oleic acid is $C_{17}H_{33}COOH$.
- Molar atomic mass in g.mo^{-1}: H = 1; C = 12; O = 16; Na = 23.
- Hard water contains appreciable quantities of Ca^{2+} and Mg^{2+} ions.
- In France, water hardness is expressed in hydrotimetric degree (°TH) where 1°TH corresponds to 0.10 mol of calcium or magnesium ions in one m^3 of hard water.

I- Generalities

Soaps can be obtained by saponification of triglycerides.

1- Define saponification reaction. How does this reaction differ from the acid catalyzed hydrolysis of ester?
2- Give the general formula of a triglyceride.
3- Soaps should not be used in an acidic medium. Justify.

II- Behavior of Soap in Hard Water

On the label of a detergent, we read:

- Active ingredient: sodium oleate.
- A higher quantity of this product must be used when the used water is hard.

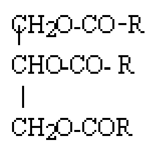
1- Give the formula and the name of the triester (triglyceride) that should be used for the preparation of the above soap.
2- Determine the mass of trigyceride that should be used to prepare 100 g of sodium oleate.
3- In order to clean a certain fabric, we use 100 g of sodium oleate and 25 L of water of 20°TH (due to Ca^{2+} only).
a) Explain what phenomenon is observed during the dissolution of the soap in the given water sample.
b) Write the equation of the reaction that translates the phenomenon observed in part (a).
c) Verify that the mass of soap which remains available for detergency action is 70 g.

Solution:

Saponification reaction corresponds to the action of a strong base (KOH or NaOH) on an ester (triglyceride).

Saponification reaction (or hydrolysis of an ester in basic medium) is complete, slow and exothermic while the acid catalyzed reaction of an ester is incomplete, slow and athermic.

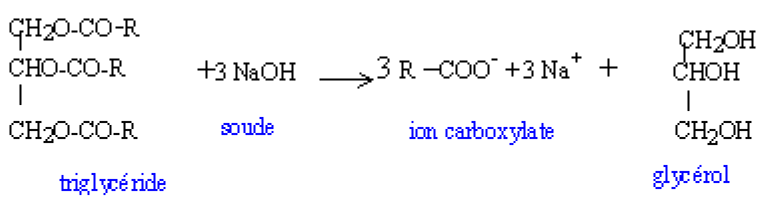
Triglyceride is a triester of glycerol and fatty acid (RCOOH where R is a long, non branched alkyl group).



$$RCOO^- + H_3O^+ \rightarrow RCOOH + H_2O$$

The acid produced is practically insoluble in the medium and it may render the solution milky (turbid). Since the $RCOO^-$ ions are consumed by the reaction, then the detergency power of the soap diminishes. So it is recommended not to use soap in acidic medium.

Let R be $C_{17}H_{33}$ then the saponification reaction of this triglyceride (olein) with NaOH is given by this reaction:



According to the coefficients of the above reaction:

n (sodium oleate) = 3 ×n (olein)

m (olein) = 100g; M (olein) = 884 $g.mol^{-1}$; M (sodium oleate) = 304 $g.mol^{-1}$.

Thus m (olein) = 97 g.

A precipitate is observed due to the reaction between oleate ions and Ca^{2+} ions.

$$2\,(C_{17}H_{33}COO^-, Na^+)_{(aq)} + Ca^{2+}_{(aq)} \rightarrow (C_{17}H_{33}COO)_2Ca_{(s)} + 2\,Na^+_{(aq)}$$

The formed calcium oleate is insoluble. The oleate ions which are responsible about the detergent properties become fewer in solution.

First step: determination of the number of moles of Ca^{2+} ions in 25 L hard water.

1°TH corresponds to 0.10 mol of Ca^{2+} ions in 1 m^3 of water. So 20°TH will correspond to 2 mol of Ca^{2+} ions in 1 m^3 (1000 L) of water.

Thus the quantity of mole of Ca^{2+} ions in 25 L is $(25\times2) / 1000 = 5\times10^{-2}$ mol.

Second step: determination of the quantity of sodium oleate that has reacted with Ca^{2+} to form the precipitate.

According to the coefficients of the reaction of part (II-3-b): n (oleate) = 2 × n (Ca^{2+}) = 0.1 mol.

Third step: Computing the mass of oleate remains for detergency action.

$n_{remain} = n_{initial} - n_{reacted}$ with $n_{initial} = m / M = 100 / 304 = 0.33$ mol

So $n_{remain} = 0.1 - 0.33 = 0.23$ mol.

Thus m (soap) $_{remain} = n \times M = 0.23 \times 304 = 70$ g.

Second Exercise
pH of a Mixture

The aim of this exercise is to calculate the pH of a mixture of two solutions of known pH.

Given: pKa_1 (HNO_2 / NO_2^-) = 3.3; pKa_2 ($HCOOH$ / $HCOO^-$) = 3.8; pK_w = 14

I - Study of Two Aqueous Solutions

The pH of nitrous acid (HNO_2) solution of concentration $C_1 = 0.20$ mol.L^{-1} is found to be $pH_1 = 1.3$ and that of sodium methanoate (HCOONa) solution of molar concentration $C_2 = 0.40$ mol.L^{-1} is found to be $pH_2 = 8.7$.

1. Write the equation of the reaction between nitrous acid and water and give the expression of its equilibrium constant.
2. Write the equation of the reaction between methanoate ion and water and give the expression of its equilibrium constant.
3. Trace, on the pH axis, a diagram of predominance of the two acid/base couples involved. Deduce the predominant species in each of the two preceding solutions.

II- Determination of pH of a Mixture of the Two Solutions

1. We mix the same volume v = 200 mL of each of the two preceding solutions. The quantity of matter of nitrous acid introduced into the mixture is $n_1 = 4 \times10^{-2}$ mol and that of sodium methanoate is $n_2 = 8 \times10^{-2}$ mol.

    a) Write the equation of the reaction which occurs between nitrous acid and methanoate ions.
    b) Express, then calculate, the quotient of the reaction $(Q_r)_i$ of the system in the initial state.
    c) Calculate the quotient of the reaction $(Q_r)_{eq}$ of the system at equilibrium. Deduce the direction of evolution of the reaction written in (1.a).

2. At equilibrium, the quantitry of NO_2^- (or HCOOH) formed is $x_{eq} = 3.3 \times 10^{-2}$ mol.

   a) Calculate the concentrations of the chemical species that present at equilibrium.
   b) Deduce $(Q_r)_{eq}$ and compare it with the value obtained in question (1. c).

3. Verify that the value of the pH of the mixture is 4.

Solution:

- *Equation of the reaction between nitrous acid and water:*

$$HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$$

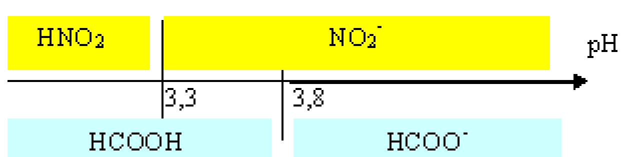
- *Acidity constant*: $K_{a1} = [H_3O^+]\,[NO_2^-] / [HNO_2]$

- *Equation of the reaction between methanoate ion and water:*

$$HCOO^- + H_2O \rightleftharpoons HCOOH + HO^-$$

- *Expression of equilibrium constant*: $K = ([HCOOH]\,[HO^-]) / [HCOO^-]$

- *Domain of predominance of the two acid-base couples involved:*



- *Predominant species of each of the two solutions*:

At pH =1.3 (value less than pK_{a1}), the nitrous acid predominates; at pH = 8.7 (value greater than pK_{a2}), methanoate ions predominate.

- *Equation of the reaction between nitrous acid and methanoate ions:*

$$HNO_2 + HCOO^- \rightarrow NO_2^- + HCOOH$$

- *Quotient Q_{ri} of the above reaction:*

$Q_{r,i} = ([NO_2^-]_i[HCOOH]_i) / ([HNO_2]_i[HCOO^-]_i) = 0$ since $[NO_2^-]_i = [HCOOH]_i = 0$

- *Expression of $Q_{r\ eq}$ in terms of equilibrium constants of the couples:*

$Q_{r\ eq} = ([NO_2^-]_{eq} [HCOOH]_{eq}) / ([HNO_2]_{eq}[HCOO^-]_{eq})$

$= ([NO_2]_{eq}[HCOOH]_{eq}[H_3O^+]_{eq}) / ([HNO_2]_{eq}[HCOO^-]_{eq}[H_3O^+]_{eq})$

$Q_{r,eq} = K_{a1} / K_{a2} = 10^{-3.3} / 10^{-3.8} = 10^{0.5} = 3.2.$

- *Sense of evolution of the reaction*:

$Q_{r,i} < Q_{r,eq}$, thus the evolution is in the forward direction.

	HNO_2	$+ HCOO^-$	$\rightarrow NO_2^-$	$+ HCOOH$
initial	$n_1 = 4 \times 10^{-2}$	$n_2 = 8 \times 10^{-2}$	0	0
At equilibrium	$n_1 - x_{eq}$	$n_2 - x_{eq}$	x_{eq}	x_{eq}
$x_{eq} = 3.3 \times 10^{-2}$	7×10^{-3}	4.7×10^{-2}	3.3×10^{-2}	3.3×10^{-2}

- *Concentration of the species at equilibrium:*

Volume of mixture = 0.4 L

$[HNO_2]_{eq} = 7 \times 10^{-3} / 0.4 = 1.8 \times 10^{-2}$ mol.L^{-1}.

$[HCOO^-]_{eq} = 4.7 \times 10^{-2} / 0.4 = 0.12$ mol.L^{-1}.

$[NO_2^-]_{eq} = [HCOOH]_{eq} = 3.3 \times 10^{-2} / 0.4 = 8.3 \times 10^{-2}$ mol.L^{-1}.

- *Deduction of $Q_{r,(eq)}$:*

$Q_{r,(eq)} = (8.3 \times 10^{-2})^2 / (0.12 \times 1.8 \times 10^{-2}) = 3.2.$

This value is identical to that obtained above.

- *pH of the mixture:*

$pH = pK_{a2} + \log ([HCOO^-]_{eq} / [HCOOH]_{eq}) = 3.8 + \log (0.12 / 8.3 \times 10^{-2}) = 4$

Third Exercise

Kinetics of Self Oxidation-Reduction of Sodium Thiosulfate

Hydrated sodium thiosulfate, $Na_2S_2O_3.2H_2O$, is a white solid. The aim of this exercise is to study the kinetics of the self oxidation-reduction reaction of sodium thiosulfate solution in a strong acidic medium, according to the following equation:

$$\mathbf{S_2O_3^{2-}{}_{(aq)} + 2\,H_3O^+{}_{(aq)} \rightarrow S_{(s)} + SO_{2\,(aq)} + 3\,H_2O_{(l)}}$$

<u>Given</u>:

Molar mass in $g.mol^{-1}$: $M_{(H)} = 1$; $M_{(O)} = 16$; $M_{(Na)} = 23$; $M_{(S)} = 32$.

I- <u>Preparation of a Sodium Thiosulfate Solution</u>

A volume of 250 mL of sodium thiosulfate solution of concentration $C = 0.5\ mol.L^{-1}$ is to be prepared.

1- Determine the mass of hydrated sodium thiosulfate needed for this preparation.
2- Choose, from the list below, the appropriate material needed to perform this preparation:
   - Sensitive balance
   - 10 and 20 mL volumetric pipettes
   - 250 and 500 mL beakers
   - spatula
   - 250 and 500 mL volumetric flasks
   - watch glass
   - Burette
   - 50 mL and 100mL graduated cylinders
   - Funnel

II- <u>Preliminary Study</u>

At time t = 0, 10 mL of 5 $mol.L^{-1}$ hydrochloric acid solution is placed into a beaker containing 40 mL of a sodium thiosulfate solution of concentration $C = 0.5\ mol.L^{-1}$. With time, suspended fine solid particles are progressively formed.

1- Determine the concentrations $[S_2O_3^{2-}]_i$ and $[H_3O^+]_i$ in the reaction mixture at t = 0.
2- Determine the limiting reagent. Deduce the quantity of sulfur produced at t = ∞.

III- <u>Kinetic Study</u>

The kinetics of the given reaction is studied by measuring the concentrations of $S_2O_3^{2-}$ remained in the reaction mixture at different instants. The results are given in the following table:

t (s)	**0**	**15**	**30**	**45**	**60**	**90**	**120**	**180**	**240**	**300**
$[S_2O_3^{2-}]$ mol.L^{-1}	**0.4**	**0.33**	**0.26**	**0.2**	**0.167**	**0.11**	**0.06**	**0.028**	**0.017**	**0.014**
$n_S \times 10^{-3}$										

1- Show, at each instant t, that the quantity of sulfur formed, expressed in mol, is given by the following expression: $\mathbf{n_{S\,(t)} = 0.02 - 0.05\,[S_2O_3^{2-}]_t}$.
2- Rewrite and complete, on the answer sheet, the above table.
3- Plot, on a graph paper, the curve $n_S = f(t)$. Take these scales: *abscissa:* 1 cm for 40 sec; *ordinate:* 1 cm for 2.5×10^{-3} mol.
4- Determine the half-life of the reaction.

Solution:

I-1)

To prepare this solution, we need n = C x V mol of $Na_2S_2O_3.2H_2O$ of m = C x V X M, with: M = (2×23) + (2×32) + (3×16) + (2×18) = 194 g.mol^{-1}.

So: $m = 0.5\times250\times10^{-3}\times194 = 24.25$ g.

I-2)

The needed material to carry out this preparation includes: sensitive balance, 500 mL volumetric flask, funnel, watch-glass and spatula.

II-1)

$[S_2O_3^{2-}]_i = (40 \times 0.5) \div 50 = 0.4$ mol.L^{-1} and $[H_3O^+]_i = (10 \times 5) \div 50 = 1$ mol.L^{-1}

II-2)

Ratio of $S_2O_3^{2-}$ = 0.4 / 1 is less than Ratio of H_3O^+ = 1 / 2 (ratio is 1:2)

So $S_2O_3^{2-}$ is the limiting reagent.

According to the coefficients of reaction:

$n_{S\text{ (formed at the end of reaction)}} = n_0(S_2O_3^{2-}) = 40\times0.5\times10^{-3} = 0.02$ mol

III-1)

Based on the equation of the reaction:

$n(S_2O_3^{2-})_{\text{reacting}} = n(S)_{\text{formed}} = n(S_2O_3^{2-})_{\text{at t = 0}} - n(S_2O_3^{2-})_{\text{remaining at t}}$

$n(S_2O_3^{2-})_{\text{at t = 0}} = 0.02$ mol and $n(S_2O_3^{2-})_{\text{remaining at t}} = [S_2O_3^{2-}]_t\times V_{\text{mixture in L}} = 0.05\,[S_2O_3^{2-}]_t$

Thus $\mathbf{n_{S\,(t)} = 0.02 - 0.05\,[S_2O_3^{2-}]_t}$

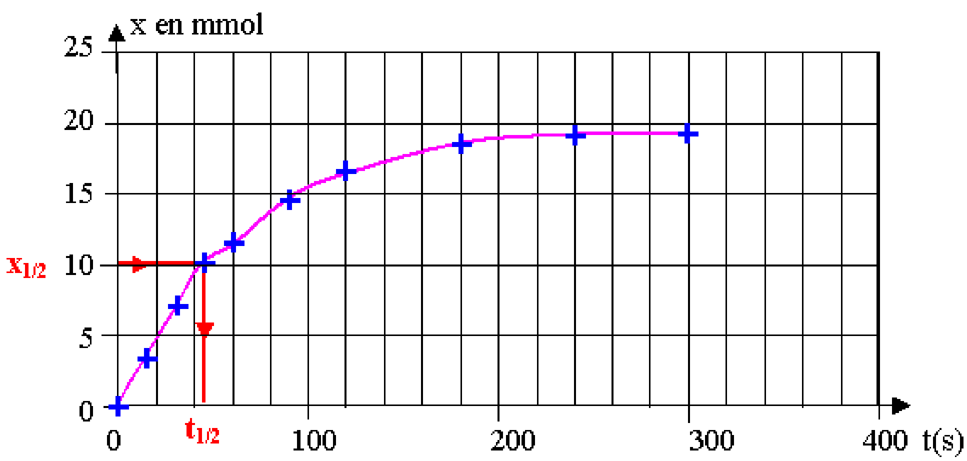
III-2)

t (sec)	0	15	30	45	60	90	120	180	240	300
$10^{-3} \times n_S$	0	3.5	7	10	11.5	14.5	16.5	18.5	19.1	19.3

III-4)

The half life is the time at which $n_{(S)} = 0.5 \times n_{S\ (\text{formed at the end of reaction})} = 0.01$ mol

So from the graph we get $t_{1/2} = 45$ sec.



Economy Sample
First Exercise
Breast Milk- the Best Start

Breast milk is the perfect start for your baby as they'll get all the nourishment they need. Just as importantly, breast milk also strengthens your baby's immune system to protect against a range of illnesses, particularly when they're most weak (the first six months). Breast milk is the natural and also the best diet for infants during the first months of life. It provides babies with everything they need for their optimal physical and mental development.

What are the protective benefits of breast milk?

- It prevents stomach upset and diarrhea.
- It prevents chest and ear infections.
- It protects against allergies like eczema and asthma, particularly if other members of the family already suffer from them.
- It helps in reducing other immune diseases like inflammatory bowel (intestine) disease.

It's well known that breastfed babies get fewer infections and allergies than formula-fed babies. This is because breast milk naturally strengthens baby's immune system. One of the reasons for this is that breast milk contains "prebiotics". There are millions of "good" bacteria in your baby's intestine such as "intestinal floras", which are micro-organisms that live in the intestine. Prebiotics act as food for them so that they flourish and increase in numbers. The "good" bacteria encourage a protective lining to form in your baby's intestine. These bacteria activate and strengthen the immune system, inhibit the growth of potentially harmful bacteria and support absorption and digestion of nutrients. That is why breast milk really is the best start you can give your baby. As time goes by, your baby's needs will change- and breast milk adapts to keep meeting them.

Composition of one liter of mother's milk		Given:
Minerals (phosphorous, calcium, …)	7g to 9g	Energy value for 1 g of nutrient:
Carbohydrates(Lactose)	45g to 50g	Carbohydrates:17 kJ;
Lipids	33g to 47g	Lipids: 38 kJ;
Proteins	32g to 36g	Proteins: 17 kJ.
water	870g to910g	

For many babies and people, digestion and absorption of lactose cause a problem. It is due to deficiency in the enzyme lactase that may arise from a genetic defect, the diminishing of this enzyme with age or the injuries of the mucus lining the intestine

Questions:

1- Give the names the chemical elements that constitute lactose.
2- Indicate the class of lactose.
3- Write the word equation of hydrolysis of lactose, and specify the class of each of the products. Specify whether this reaction is catabolic or anabolic reaction.
4- Use the above text to:
a) Give the name of "good" bacteria.

b) Mention two benefits for the “good” bacteria in the baby’s body.
c) Explain the statement “Breast milk helps in the development of good bacteria”.
d) Justify why mother’s milk is considered as a complete food.
e) Justify that babies who are breastfed develop better and healthier than formula-fed babies.

5- Determine the maximum energy value of one liter of mother’s milk.

Second Exercise
Pedimax®
Enfants Vitamins and Minerals

Vitamins and Minerals are a daily need to ensure the normal functions of our body. To secure healthy growth, it is particularly important that children get enough of the essential vitamins and minerals. Such essentials enhance the development of the brain and body and improve your child’s ability to learn and study.

Children get nutrients from the food they eat, yet many do not get the sufficient amount. Children tend to like fast food, whereby the nutritious values are limited. Further, with new agricultural techniques, even fruits and vegetables contain reduced amounts of vitamins and minerals.
It is very important that you teach your child to eat a variety of healthy food, but a vitamin “safety net” in the form of a daily multivitamin tablet, could spare you some worries during your child’s early years.

If you feel that your child is often: tired, nagging, sensitive, irritable, violent, has a weak immune system, often tend to be ill, or has learning /behavioral problems; it might be signs of vitamin deficiency.

Vitamin deficiency is a serious problem; many diseases can result from this deficiency. Scurvy is a disease that is characterized by a slight fever, anemia and multiple hemorrhages especially at the level of gums which becomes spongy and inflamed, loose teeth and intestinal troubles. A food rich in oranges and lemons is recommended for a child attacked by this disease.

Rickets is manifested by skeletal deformities, gastro-intestinal troubles it is a deficiency disease of children and adolescents encountered during growth periods, due to the lack of sufficient vitamin D in the diet or to insufficient ultra violet radiation from direct sunlight.
Pedimax Multivitamin will supplement all the necessary vitamins and minerals and regulate any potential deficiency.

Nutrition information per tablet

	RDA*		RDA*
Vitamin A	400µg =100%	Copper	0.4mg=100%
Thiamin (B_1)	0.7mg=100%	Iodine	70 µg=100%
Folic acid (vitamin B_9)	75 µg=100%	Zinc	5mg=100%
Vitamin C	40mg=100%	Magnesium	21.5mg=25%
Vitamin D	10 µg=100%	Iron	8mg=100%
Vitamin E	5mg=100%	Calcium	100mg=17%

RDA*: Recommended Daily Amount

Walnuts, hazelnuts and almonds have interesting properties. The only negative side about them is that they are rich in lipids, but these foods are sources of proteins, magnesium and calcium, they can contribute to a balanced diet. Their proteins are rich in arginine (amino acids) which is capable to reduce cholesterol. Chocolate is also rich in minerals. For 100g of cacao: potassium (1.920g); phosphorous (0.656g); magnesium (0.414g); calcium (0.114g)

Questions:

1- Name the vitamin which is not mentioned in the table.
2- Classify the vitamins in the table as liposoluble and hydrosoluble.
3- Referring to the given information, specify if iodine and magnesium are macro-mineral or trace mineral.
4- List four symptoms that indicate the child is suffering from deficiency in vitamins.
5- Often vitamin **E** is added to butter. Give a justification for this addition.
6- Based on the text, identify the role of Vitamin **C** and **D**. State one source for each.
7- Write the structural formula of α-amino acid, circle and name its main characteristic groups. Draw the structure of a dipeptide.
8- The average daily requirement of phosphorous for an adult is 820 mg. Calculate the mass of black chocolate containing 50% of cacao that could provide 40% of this requirement.

First Exercise (10 points)

Part	Expected Answer	Mark
1	The chemical elements that constitute lactose are carbon, hydrogen and oxygen.	0.75
2	Lactose is an oligosaccharide (disaccharide).	0.25
3	The hydrolysis reaction of lactose is: Lactose + water → glucose + galactose The products (glucose and galactose) are monosaccharides.	2.5

	The reaction is catabolic reaction since it involves the breaking down of a large molecule (lactose which is a disaccharide) into smaller molecules (glucose and galactose which are monosaccharides).	
4-a	The good bacteria are called intestinal floras.	0.5
4-b	- They strengthen the baby's immune system. - They inhibit the growth of potentially harmful bacteria. - They support absorption and digestion of nutrients.	1.5
4-c	Breast milk contains prebiotics which act as a food for the good bacteria so that they flourish and increase in numbers.	1
4-d	Mother's milk is rich in the principal nutrients: carbohydrates, lipids, proteins, minerals and vitamins, so it is described as a complete food.	1
4-e	- They strengthen the baby's immune system.	0.25
5	Maximum Energy obtained from: - Proteins: 36 x 17 = 612 kJ; - Carbohydrates: 50 x 17 = 850 kJ; - Lipids: 47 x 38 = 1786 kJ. Maximum energy produced by 100 g of milk: 850+612+1786 = 3248 kJ.	2.25

Second Exercise (10 points)

Part	Expected Answer	Mark
1	The vitamin which is not mentioned in the text is vitamin K.	0.5
2	Vitamins B_1, B_9 and C are hydrosoluble (soluble in water), non toxic, and are eliminated through urine. Vitamins A, D, and E are liposoluble (soluble in lipids), toxic and are not eliminated through urine.	1.5
3	The RDA of Mg = 21.5 × (100 / 25) = 86 mg. Although this quantity is	1.5

	less than 100 mg/day but it is far greater than 20mg /day. So Mg is a macro-mineral. The RDA of iodine is 70µg < 20 mg/day so iodine is a trace mineral.	
4	The symptoms are: irritation, nagging, violence, fatigue (feeling tired), and weak immune system, tendency to be ill, existence of learning and behavioral problems….	1
5	Vitamin E is added to butter to prevent the oxidation of lipids (it is an antioxidant).	1
6	Vitamin C prevents scurvy; it is present in lemons and oranges. Vitamin D prevents rickets; sun light is a source of vitamin D	1

7	The general structural formula of an alpha amino acid is:
	
	R – CH – COOH
	      │
	     NH_2
	
	-COOH = Carboxyl group; - NH_2 = Amino group.
	The chain of two amino acids gives a dipeptide molecule:
	
	R – CH – CO – NH – CH - COOH
	
		|
		     NH_2 R
			2

8	40 % of the daily need of phosphorus is : 820×0.4 = 328 mg = 0.238 g Corresponding mass of cocoa = 0.238 × (100/0.656) = 50 g Thus mass of cocoa = (50×100) / 50 = 100 g.	1.5