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 (7 points)
Decomposition of Hydrogen Peroxide

The commercial hydrogen peroxide is an aqueous hydrogen peroxide solution. It is used for the maintenance of the contact lenses, as a disinfecting agent, …
Hydrogen peroxide decomposes, at 25°C, in a very slow and complete reaction according to the following equation: $2\ H_2O_{2(aq)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$
Suppose that, at the conditions of the experiment, oxygen gas is insoluble in water.

1- Catalysis of this Reaction

This decomposition reaction can be accelerated by using a catalyst such a platinum wire, or an iron (III) chloride solution ($Fe^{3+} + 3\ Cl^-$).
1.1- Name the type of the catalysis carried out in the presence of a platinum wire.
1.2- The mechanism of this catalysis occurs in three steps: adsorption, reaction and desorption.
1.2.1- Assign, to each step, one of the following propositions :
- The reactants are transformed into products.
- The products escape from the surface of the catalyst.
- The reactants are attached to the surface of the catalyst.

1.2.2- Deduce the importance of the contact surface between reactants and a catalyst.
1.3- Consider a beaker containing an aqueous hydrogen peroxide solution in the presence of iron (III) chloride. Indicate the chemical species present in the solution obtained at the end of the decomposition reaction.

2- Kinetic of the Decomposition Reaction of H_2O_2

Nine beakers are available, each contains a volume V_0 = 20.0 mL of a hydrogen peroxide solution of concentration C_0, in the presence of few drops of the iron (III) chloride solution.
The remaining hydrogen peroxide in each one of the beakers is titrated, at different instants, with an acidified potassium permanganate solution, of concentration $C = 2.0\times10^{-2}$ mol.L^{-1}.
The equation of the titration reaction is:

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 8\ H_2O$$

The volume of the permanganate solution, added to reach the equivalence point in each beaker is determined. The concentration of H_2O_2, remained in V_0, at the instant t, is deduced.
The results are grouped in the following table:

t (min)	0	3	6	9	15	21	27	33	39
$[H_2O_2]$ (10^{-2} mol.L^{-1})	-	4.2	3.5	2.9	2.0	1.4	1.0	0.70	0.50

2.1- Choose, from the following list, the material needed to carry out this titration:
pH-meter and its electrode, stand, magnetic stirrer and its bar, 100 mL graduated cylinder, 100 mL volumetric flask and 50 mL graduated buret.

2.2- Before starting the titration, icy- water is poured into each beaker.

2.2.1- Indicate the two kinetic factors involved in this operation.

2.2.2- Specify the effect of each one of these two factors on the kinetic of the decomposition reaction of hydrogen peroxide.

2.3- Show that the initial concentration of the hydrogen peroxide solution is $C_0 = 5.0\times10^{-2}$ mol.L^{-1}, knowing that the volume of the potassium permanganate solution added to reach the equivalence point at t = 0 is V_E = 20 mL.

2.4- Plot the curve representing the variation of the concentration of H_2O_2 versus time: $[H_2O_2]$ = f (t), in the time interval [0 – 39 min].
Take the following scale: 1 cm for 3 min in abscissa,
1 cm for 5.0×10^{-3} mol.L^{-1} in ordinate.

2.5- Determine the rate of disappearance of H_2O_2 at the instant t = 18 min. Deduce the rate of the reaction at this instant.

Second Exercise (6 points)
α-Amino acids and Peptides

Proteins and peptides enter in the constitution of the living organisms and take part in their operation while intervening in a large number of biochemical reactions. They are macromolecules obtained by the association of α-amino acids linked by peptide bond.

<u>Given</u>

- Molar Mass in g.mol^{-1}: M (H) = 1; M (C) = 12; M (N) = 14; M (O) = 16.

1- Identification of an α-Amino acid (A)

The analysis carried out on an α-amino acid (A) shows that:

- Its molecule contains only one nitrogen atom.
- The mass percentages of its elements are:
  % C = 40.45; % H = 7.87; % N = 15.72 and % O = 35.96

1.1- Show that the molecular formula of the acid (A) is $C_3H_7NO_2$.

1.2- Write its condensed structural formula and give its systematic name.

1.3- Represent, according to Cram, the two enantiomers of the acid (A).

2- Formation of the Dipeptide

A dipeptide (D) is prepared by the condensation reaction between one molecule of the acid (A) and one molecule of an α-amino acid (B) of formula:

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H2N– CH – COOH
      |
      R
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where, R is an alkyl radical.

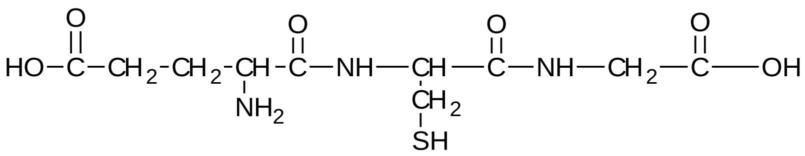
2.1- Show that the formula of R is C_4H_9 knowing that the molar mass of the dipeptide formed is equal to 202 g.mol^{-1}.

2.2- Write the condensed structural formula of the acid (B) knowing that its molecule contains two asymmetric carbon atoms. Give its systematic name.

2.3- Write the two possible condensed structural formulas of (D).

3- *α*-Amino acids Constituting Glutathione

Glutathione is a tripeptide which plays a regulatory role in the oxidation reduction reaction in animal cells. The condensed structural formula of glutathione is:



3.1- Give the number of the peptide bonds in the glutathione molecule.
3.2- Write the condensed structural formula of an acid produced from the hydrolysis of this tripeptide.

Third Exercise (7 points)
Study of a Household Product

The indications on a label of the flask of a household product are not readable any more.
This product is one of the three following aqueous solutions: sodium hydroxide, ammonia or acetic acid.
In this exercise, it is required to identify the solute of this household product and to determine, using pH-metric follow-up, its concentration.
Given:

- The study is carried out at 25 ºC.
- Ammonia is a weak base.
-

Acid/base pair	H_3O^+/H_2O	CH_3COOH/CH_3COO^-	NH_4^+ / NH_3	H_2O/HO^-
pKa	0.0	4.8	9.2	14.0

1- Identification of the Solute of the Household Product

The measurement of the pH of this product gives a pH = 10.6
1.1- Draw,from this measurement, the conclusion concerning the identification of the solute of this household product.
1.2- A sample of this product is diluted 10 times, a solution of pH′ = 10.1 is obtained. Deduce that this solute is ammonia.
1.3- Write the equation of the reaction between ammonia and water.

2- Titration of the Household Product

A volume V_B = 10.0 mL of the household product is poured into a 250 mL beaker, and distilled water is added to immerse properly the pH-meter electrode.
A pH-metric titration is then carried out, by adding gradually, a hydrochloric acid solution of concentration C_a = 0.010 mol.L^{-1} into the beaker.
The volume of the acid solution added to reach equivalence is V_{aE} = 12.7 mL.
2.1- Write the equation of this titration reaction.
2.2- Justify the use of this fast reaction as a titration reaction.
2.3- Determine the concentration of ammonia in this household product.
2.4- For this pH-metric titration and its results, five statements are suggested.

When the statement is true, justify it.
When the statement is false, give the right answer.

2.4.1- The hydrochloric acid solution is added gradually using a 25 mL graduated cylinder.

2.4.2- The pH of the solution in the beaker, just before the addition of the acid solution, is equal to 10.6

2.4.3- The medium obtained at equivalence is acidic.

2.4.4- The pH of the mixture obtained for a large addition of the acid solution tends towards zero.

2.4.5- The pK_a of the conjugate pair NH_4^+ / NH_3 is given by the following relation:

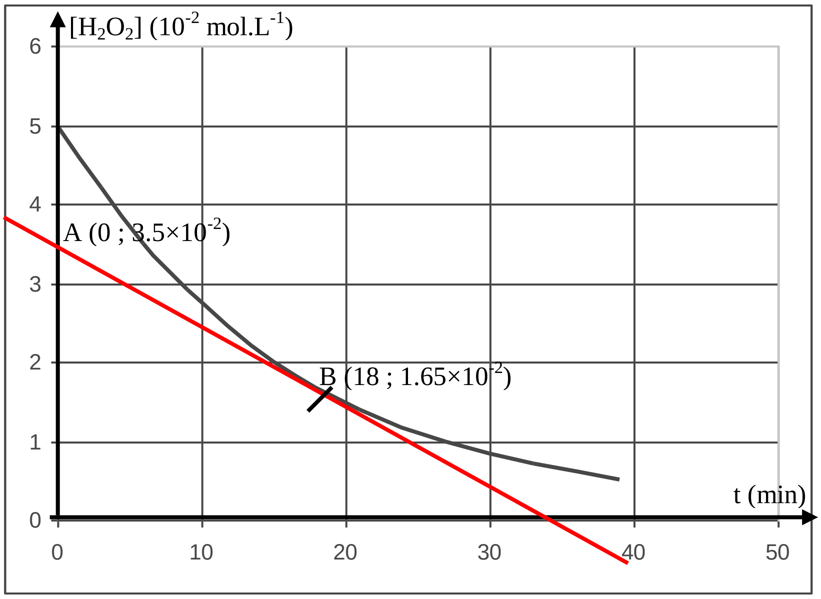
$$pK_a = pH - \log \frac{V_{aE} - V_a}{V_a} \;;$$

where V_a is the volume of the acid solution added before the equivalence, and the pH is the pH of the mixture obtained at the time of this addition.

مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة ساعتان	الاسم: الرقم:

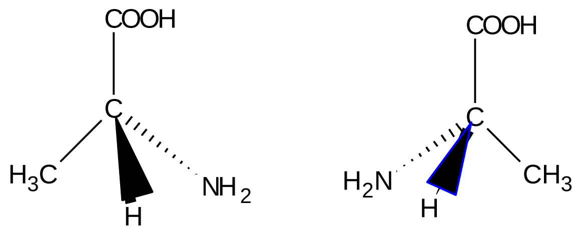
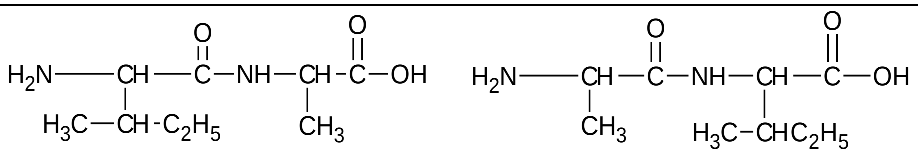
Answer the three following exercises:

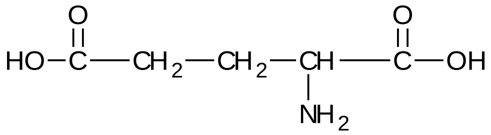
First exercise (7 points)

Part of the Q	Answer	Mark
1.1	The catalysis carried out with a platinum wire is a heterogeneous catalysis.	**0.25**
1.2.1	Adsorption: The reactants are attached to the surface of the catalyst. Reaction: The reactants are transformed into products. Desorption: The products escape from the surface of the catalyst.	**0.75**
1.2.2	As long as the contact surface: reactant-catalyst, increases, as long as the rate of the reaction is higher.	**0.5**
1.3	The species present in the solution at the end of the decomposition reaction are: H_2O, Fe^{3+} and Cl^-.	**0.75**
2.1	The material needed: 50 mL graduated buret, stand, magnetic stirrer and its bar.	**0.75**
2.2.1	The two kinetic factors involved in this operation are: temperature of the reaction medium and the concentration of the reactant H_2O_2.	**0.5**
2.2.2	In this operation, the temperature decreases and $[H_2O_2]$ decreases. The rate of the reaction will decrease in such a way that the reaction will be practically blocked.	**0.5**
2.3	At the equivalence point: $\frac{n(MnO_4^-)\,\text{added}}{2} = \frac{n(H_2O_2)\,\text{initial in the beaker}}{5}$; $\frac{C \times V_E}{2} = \frac{C_0 \times V_0}{5}$; $C_0 = \frac{5 \times C \times V_E}{2 \times V_0} = \frac{5 \times 0.02 \times 20}{2 \times 20} = 5.0\times10^{-2}\ mol.L^{-1}$.	**0.75**
2.4	The curve is:  	**1**

2.5	By definition, r (H_2O_2) = - $\frac{d[H_2O_2]}{dt}$. Graphically, this rate is the negative slope of the tangent to the curve at the point of abscissa 18 min. Choose on this tangent the two points A and B such as: A (0; 3.5×10^{-2} mol.L^{-1}) and B (18 min ; 1.65×10^{-2} mol.L^{-1}). So r (H_2O_2) = - $\frac{0.035-0.0165}{0-18}$ =1.03×10^{-3} mol.L^{-1}.min^{-1}. The reaction rate at the same instant is: $r_{rxn} = \frac{1}{2}$ r (H_2O_2) = $\frac{1.03\times10^{-3}}{2}$ = 0.501×10^{-3} mol.L^{-1}.min^{-1}.	**1.25**

Second exercise (6 points)

Part of the Q	Answer	Mark
1.1	The sum of the percentages = 100 %, implies the molecular formula of A does not contain other elements than C, H, O, and N. The molecular formula of A is of the form $C_xH_yO_zN$. The law of the definite proportions makes it possible to write: $\frac{12x}{\%C} = \frac{y}{\%H} = \frac{16z}{\%O} = \frac{14}{\%N}$; $\frac{12x}{40.45} = \frac{y}{7.87} = \frac{16z}{35.96} = \frac{14}{15.72}$. x = $\frac{40.45\times14}{12\times15.72}$ = 3; y = 7; z = 2. The molecular formula of A is $C_3H_7O_2N$	1
1.2	Since A is an α-amino acid its condensed structural formula is then: CH_3 – CH – COOH ; it is 2-aminopropanoic acid (with NH_2 on CH)	0.75
1.3	The two enantiomers of A are:  	0.75
2.1	M(B) = M(D) + M(H_2O) – M(A) = 202+18-89= 131g.mol^{-1}. But M(B) = M(R) + 74 with R: C_nH_{2n+1} 14n = 56; n = 4. The formula of R is: C_4H_9.	1
2.2	The formula of B having two asymmetrical carbon atoms is: C_2H_5 – CH – CH – COOH; it is 2-amino-3-methylpentanoic acid. (with CH_3 on the first CH and NH_2 on the second CH)	0.75
2.3	 	1
3.1	There are two peptide bonds in this tripeptide.	0.25

3.2	One of the acids produced is: 	0.5

Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	pH = 10.6 > 7 : basic medium, means that the solute is not acetic acid; it is either sodium hydroxide solution or ammonia solution.	**0.5**
1.2	Since the decrease in the pH is less than one unit; the solute is not a strong base, it is a weak base which is the ammonia.	**0.5**
1.3	The equation of the reaction between ammonia and water is : $NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$	**0.5**
2.1	The equation of the titration reaction between ammonia and H_3O^+ ions is: $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$.	**0.5**
2.2	The reaction constant of this reaction: $K_r = \frac{[NH_4^+]}{[NH_3].[H_3O^+]} = \frac{1}{K_a(NH_4^+/NH_3)} = 10^{9.2} > 10^4$; this fast reaction is complete, therefore we can use it as a titration reaction.	**0.75**
2.3	At the equivalence point: $n(H_3O^+)_{\text{added to reach equivalence}} = n(NH_3)_{\text{in the volume Vb}}$ $C_a.V_{aE} = C_b.V_b$ The concentration of this ammonia product is: $C_b = \frac{C_a \times V_{aE}}{V_b} = \frac{0.01 \times 12.7}{10} = 1.27 \times 10^{-2}$ mol.L^{-1}.	**1**
2.4.1	This statement is false; the acid solution is added using a graduated buret.	**0. 5**
2.4.2	This statement is false; the initial pH is <10.6 because the ammonia solution is diluted.	**0.5**
2.4.3	This statement is true; the medium at equivalence is acidic, because the species present are: Cl^-(spectator ion), H_2O and NH_4^+ which makes the medium acidic by its reaction with water.	**0.5**
2.4.4	This statement is false; for a large addition of acid solution the pH of the mixture tends towards the pH of the added solution. The pH tends towards: $-\log C_a = -\log 0.01 = 2.0$	**0.75**
2.4.5	This statement is true; before equivalence, - H_3O^+ is the limiting reactant. - there is a mixture of NH_3 and NH_4^+ - $[NH_3] = \frac{C_b \times V_b - C_a \times V_a}{V_a + V_b} = \frac{C_a \times V_{aE} - C_a \times V_a}{V_a + V_b}$ and $[NH_4^+] = \frac{C_a \times V_a}{V_a + V_b}$ $pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$; $pK_a = pH - \log \frac{[NH_3]}{[NH_4^+]} = pH - \log \frac{V_{aE} - V_a}{V_a}$.	**1**