

دورة العام 2012 الاستثنائية	امتحانات الشهادة الثانوية العامة الفرع : علوم الحياة	وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات
الاسم: الرقم:	مسابقة في مادة الكيمياء المدة : ساعتان	

**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)  
Ammonia Solution**

Ammonia  $\text{NH}_3$  is a gas which is highly soluble in water. It is widely used in chemical industry. The aim of this exercise is to study certain characters of a solution of ammonia  $\text{NH}_3$  and to prepare a buffer solution.

**Given:**

- This study is carried at 25 °C.
- Molar volume of gas:  $V_m = 24 \text{ L.mol}^{-1}$ .
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Acid/base Couple	$\text{H}_3\text{O}^+ / \text{H}_2\text{O}$	$\text{NH}_4^+ / \text{NH}_3$	$\text{H}_2\text{O} / \text{HO}^-$
$\text{pK}_a$	0	9.2	14

**1- Determination of the degree of conversion of Ammonia in Water**

The pH of an ammonia solution (S), of unknown concentration  $C_b$ , is equal to 10.6

- 1.1- Identify the acid-base nature of  $\text{NH}_3$  in water.
- 1.2- Write the equation of the reaction of ammonia with water.
- 1.3- Give the expression of the equilibrium constant of the equation of this reaction.  
Calculate its value.
- 1.4- Show that the molar concentration of ammonia solution (S) is  $C_b = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$ .  
(neglect  $[\text{HO}^-]$  with respect to  $C_b$ )
- 1.5- Determine the degree of conversion of ammonia in water.
- 1.6- Calculate the volume of  $\text{NH}_3$  gas needed to prepare 1 L of solution (S).

**2- Preparation of a Buffer Solution**

A volume  $V_1$  of solution (S) and a volume  $V_2$  of an ammonium chloride solution ( $\text{NH}_4^+ + \text{Cl}^-$ ) of concentration  $C_a = 6.0 \times 10^{-3} \text{ mol.L}^{-1}$  are mixed . 200 mL of a buffer solution of  $\text{pH} = 9.0$  is obtained .

- 2.1- Write the equation of the predominant reaction ( having the highest value of  $K_R$  ).
- 2.2- Show that  $V_1$  equals 55 mL.

2.3- To the obtained buffer solution,  $5.0 \times 10^{-4}$  mol of HCl (strong acid) is added, without appreciable variation of volume.

2.3.1- Write the equation of the complete reaction that takes place.

2.3.2- Determine the pH of the resulting solution.

### Second exercise (6 points) Creation of an ester and amide functions

Available are organic compounds having the following condensed structural formulas:

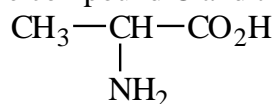
Compound	A	B	C
Condensed structural formula	$\text{CH}_3 - \text{CO}_2\text{H}$	$\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{OH}$	$\text{NH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$

In this exercise we study some chemical reactions where these compounds are involved.

- 1- Give the systematic name of the compounds A, B and C.
- 2- Choose, among these compounds, the one which is chiral. Justify.
- 3- A mixture of 0.2 mol of A and an excess of the compound B is heated. After a certain time, heating is stopped and the number of moles of the acid remaining is titrated; it is found to be 0.08 mol.
  - 3.1- Write the equation of the reaction between A and B. Name the organic product obtained.
  - 3.2- Determine the percentage of esterification of the compound A in this reaction.
- 4- An equimolar mixture of the compound A and of ammonia,  $\text{NH}_3$ , is introduced into a beaker. An ionic compound D is formed.

At high temperature, the compound D decomposes to form an amide.

  - 4.1- Write the equation of the formation of the compound D. Name this compound.
  - 4.2- Verify if this reaction is an acid-base reaction.
  - 4.3- Identify the amide formed during the decomposition of D.
- 5- In appropriate conditions, we allow the reaction between any carboxyl group and any amine group in a mixture containing the compound C and the alpha amino acid of formula:



- 5.1- Give the number of dipeptides obtained in this reaction (without taking in consideration the enantiomers).
- 5.2- Write the condensed structural formula of one of these dipeptides and circle its peptide bond.

### Third exercise (7 points) Oxidation of Oxalic Acid

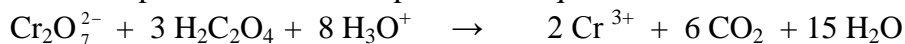
In order to carry out two kinetic follow-ups, the following solutions are available:

- Solution S<sub>1</sub> of oxalic acid H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> of concentration C<sub>1</sub> = 0.10 mol.L<sup>-1</sup>
- Solution S<sub>2</sub> of potassium dichromate ( 2K<sup>+</sup> + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> )
- Solution S<sub>3</sub> of potassium permanganate ( K<sup>+</sup> + MnO<sub>4</sub><sup>-</sup> ) of concentration C<sub>3</sub> = 2.0 × 10<sup>-2</sup> mol.L<sup>-1</sup>
- Concentrated sulfuric acid.

#### 1- Oxidation of Oxalic Acid by Dichromate Ions

At a constant temperature, a volume V<sub>1</sub> of solution S<sub>1</sub>, a volume V<sub>2</sub> of solution S<sub>2</sub> and few drops of the concentrated sulfuric acid are mixed.

A slow and complete reaction takes place. The equation of this reaction is as follows:



The variation of the concentration of dichromate ions versus time is followed with an appropriate method. The variation of the concentration of Cr<sup>3+</sup> ions formed are deduced .

The results are grouped in the following table :

t (s)	10	20	40	60	100	140	180	240	300
[Cr <sup>3+</sup> ] (10 <sup>-3</sup> mol.L <sup>-1</sup> )	1.2	2.2	4.0	5.5	7.5	9.1	10.3	11.5	12.2

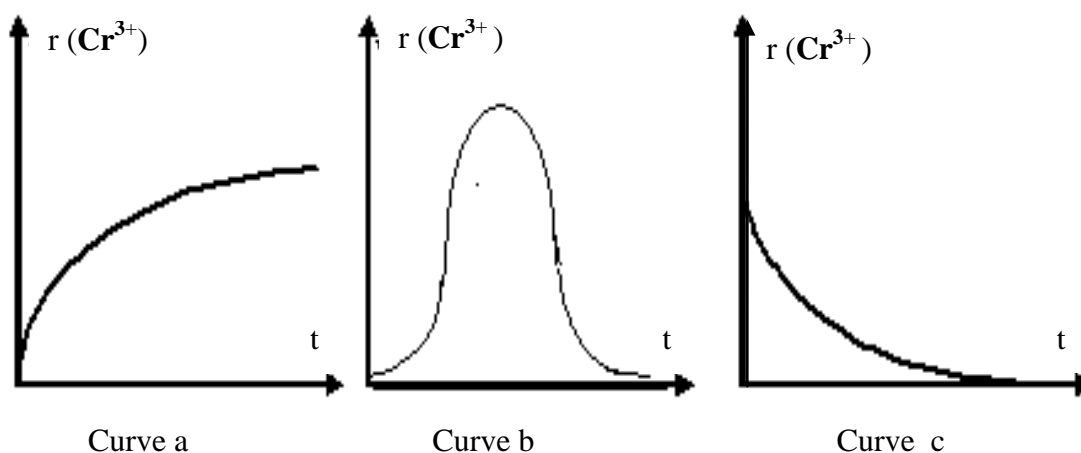
1.1- Plot the curve representing the variation of the concentration of Cr<sup>3+</sup> ions versus time, [Cr<sup>3+</sup>] = f(t) in the interval of time: [0 – 300 s].

Take the following scale: 1 cm for 20s in abscissa and 1 cm for 1.0 × 10<sup>-3</sup> mol.L<sup>-1</sup> in ordinate.

1.2- Determine the rate of formation of Cr<sup>3+</sup> ions at t = 100 s. Deduce the rate of the reaction at this instant.

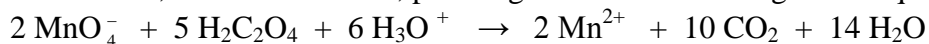
1.3- One of the three curves given below represents the variation of the rate of formation of Cr<sup>3+</sup> ions versus time, r(Cr<sup>3+</sup>) = g(t).

Choose, by justifying, the correct curve.



## **2- Oxidation of Oxalic Acid by Permanganate Ions**

Oxalic acid reduces, in acidic medium, permanganate ions according to the equation:



where  $\text{MnO}_4^-$  is the only colored species in this reacting medium.

A volume  $V_1 = 10$  mL of solution  $S_1$ , 200 mL of distilled water and 5 mL of concentrated sulfuric acid (in excess) are poured in a beaker.

Add 2 mL of solution  $S_3$  to the beaker ; the reacting mixture is decolorized when the duration 210s is attained . The addition of 2ml of solution  $S_3$  is repeated 6 times and the duration necessary for the decolorization of the reacting medium each time is noted .

The results are grouped in the following table:

Number of addition	1	2	3	4	5	6	7
Duration (s)	210	90	60	55	47	40	34

2.1- Interpret the decolorization of the reacting medium after each addition.

2.2- Determine the minimal volume of solution  $S_3$ , needed to be added, so that the color due to permanganate ions persists definitively.

2.3- Based on the results of the above table :

2.3.1- Specify how the rate of disappearance of permanganate ions varies from one addition to another.

2.3.2- Interpret the change of this rate in this kinetic study. Give, then, the name of the involved chemical phenomenon.

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### First exercise (7 points)

Part of the Q	Answer	Mark
1.1	Ammonia (NH <sub>3</sub> ) is a base because its dissolution in water leads to a medium of which pH = 10.6 > 7.	0.5
1.2	The equation of its reaction with water is: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{HO}^-(\text{aq})$	0.5
1.3	The equilibrium constant of the equation of this reaction is: $K_R = \frac{[\text{NH}_4^+][\text{HO}^-]}{[\text{NH}_3]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]}$ Its value is: $\frac{10^{-14}}{10^{-9.2}} = 10^{-4.8}$ $K_R = 1.58 \times 10^{-5}$ .	0.75
1.4	Calculation of C <sub>b</sub> : $10^{-4.8} = \frac{[\text{HO}^-]^2}{C_b - [\text{HO}^-]} = \frac{(10^{-3.4})^2}{C_b - 10^{-3.4}}$ C <sub>b</sub> = 0.01 mol L <sup>-1</sup> .	0.5
1.5	The coefficient of the dissociation α is given by: $\alpha = \frac{n(\text{NH}_3)\text{dissociated}}{n(\text{NH}_3)\text{introduced}} = \frac{[\text{NH}_4^+]}{C_b} = \frac{[\text{HO}^-]}{C_b} = \frac{10^{\text{pH}-14}}{C} = \frac{1.0 \times 10^{-3.4}}{1.0 \times 10^{-2}}$ α = 10 <sup>-1.4</sup> = 0.04	0.75
1.6	The volume of ammonia gas: V = n x V <sub>m</sub> = C <sub>b</sub> x V <sub>(S)</sub> x V <sub>m</sub> = 0.01 x 1 x 24 = 0.24 L.	0.5
2.1	The equation of the predominant reaction which takes place between the strongest acid and the strongest base introduced into the solution is: $\text{NH}_3(\text{aq}) + \text{NH}_4^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{NH}_3(\text{aq})$	0.5
2.2	The initial quantities of NH <sub>3</sub> and NH <sub>4</sub> <sup>+</sup> are conserved in the obtained solution : pH = pKa + log $\frac{[\text{NH}_3]}{[\text{NH}_4^+]}$ permits to calculate the values of the two volumes. $9 = 9.2 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}; \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = -0.2 \text{ and } \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 0.63.$ $\frac{n(\text{NH}_3)}{n(\text{NH}_4^+)} = \frac{V_1 \times 10^{-2}}{V_2 \times 6 \times 10^{-3}} = 0.63 \text{ and } V_1 + V_2 = 200 \text{ mL.}$ So V <sub>1</sub> = 55 mL.	1
2.3.1	The equation of the reaction is: $\text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.5

2.3.2	$\text{H}_3\text{O}^+_{(aq)} + \text{NH}_3_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{H}_2\text{O}_{(l)}$	1.5
Initial state(n mol)	$5.10^{-4}$ $5.5 \times 10^{-4}$ $8.7 \times 10^{-4}$ solvent	
Resulting solution	-- $5.10^{-5}$ $13.7 \times 10^{-4}$ solvent	
PH = 9.20 + log	$\frac{5 \times 10^{-5}}{\frac{V(\text{mixture})}{13.7 \times 10^{-4}}} = 7.76$	

### Second Exercise (6pts) (LS)

Part of the Q.	Answer	Mark
1	A : ethanoic acid ; B : 2-butanol et C : 2-aminoethanoic acid	0.75
2	B is the chiral compound since it contains an asymmetric carbon (the carbon number 2 of the hydrocarbon chain).	0.5
3.1	The equation of the reaction between A and B is $\text{CH}_3 - \text{CO}_2\text{H} + \text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{OH} \rightleftharpoons \text{CH}_3 - \underset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$ The name of the ester is: 1-methylpropyl ethanoate.	1
3.2	% of A esterified = $\frac{n(\text{A})_{\text{esterified}}}{n(\text{A})_{\text{initial}}} \times 100 = \frac{n(\text{A})_{\text{initial}} - n(\text{A})_{\text{remain ing}}}{n(\text{A})_{\text{initial}}} \times 100 = \frac{0.2 - 0.08}{0.2} \times 100 = 60\%$	0.75
4.1	The equation of this reaction: $\text{CH}_3 - \text{CO}_2\text{H} + \text{NH}_3 \rightleftharpoons \text{CH}_3 - \text{CO}_2^- + \text{NH}_4^+$ The name of the compound D is: ammonium ethanoate	0.75
4.2	This reaction is an acid-base reaction since there is a proton exchange between the acid of the pair $\text{CH}_3 - \text{CO}_2\text{H} / \text{CH}_3 - \text{CO}_2^-$ and the base of the pair $\text{NH}_4^+ / \text{NH}_3$	0.5
4.3	The amide formed is $\text{CH}_3 - \underset{\text{O}}{\parallel} \text{C} - \text{NH}_2$ ; its name is ethanamide	0.5
5.1	The number of dipeptides obtained in this reaction is four.	0.5
5.2	The condensed structural formula is : $\text{NH}_2 - \text{CH}_2 - \underset{\text{O}}{\parallel} \text{C} - \text{NH} - \underset{\text{CH}_3}{\text{CH}} - \text{CO}_2\text{H}$	0.75

### Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	<div style="display: flex; align-items: center;"> <div style="margin-right: 20px;">[Cr<sup>3+</sup>](10<sup>-3</sup>mo.L<sup>-1</sup>)</div> </div>	1
1.2	<p>By definition: <math>r(\text{Cr}^{3+}) = \frac{d[\text{Cr}^{3+}]}{dt}</math> at <math>t = 100</math> s.</p> <p>Graphically, this rate represents the slope of the tangent to the curve <math>[\text{Cr}^{3+}] = f(t)</math> at the point of abscissa <math>t = 100</math> s.</p> <p>Consider on this tangent two points A and B whose co-ordinates are as follows: A (0; <math>3.2 \times 10^{-3}</math>) and B (200; <math>12.0 \times 10^{-3}</math>).</p> <p>According to the equation of the reaction, we can write:</p> $r(\text{Cr}^{3+})_{t=100} = \frac{(12.0 - 3.2) \times 10^{-3}}{200} = 4.4 \times 10^{-5} \text{ mol.L}^{-1} \cdot \text{s}^{-1}.$ <p>The rate of the reaction = <math>r(\text{Cr}^{3+})/2 = 2.2 \times 10^{-5} \text{ mol.L}^{-1} \cdot \text{s}^{-1}</math>.</p>	1.5
1.3	<p>According to the curve, <math>r(\text{Cr}^{3+})</math> is maximum at <math>t = 0</math>, and decreases with time. As the reaction is complete, this rate is cancelled at the end of the reaction. Therefore, the corresponding curve is the curve <b>c</b>.</p>	1
2.1	<p>The disappearance of coloring is due to the disappearance of permanganate ions added. <math>\text{MnO}_4^-</math> is the limiting reactant.</p>	0.5
2.2	<p>The minimal volume that must be added is equal to a volume <math>V_3</math> such as:</p> $\frac{n(\text{MnO}_4^-)_{\text{added}}}{2} = \frac{n(\text{H}_2\text{C}_2\text{O}_4)_{\text{initial}}}{5} \quad \text{or} \quad \frac{C_3 \times V_3}{2} = \frac{C_1 \times V_1}{5};$ <p>Where <math>V_3 = \frac{2 \times C_1 \times V_1}{5 \times C_3} = \frac{2 \times 0.1 \times 10}{5 \times 0.02} = 20 \text{ mL}</math>.</p>	1.25
2.3.1	<p>With each addition, <math>n(\text{MnO}_4^-)</math> is the same and the duration of disappearance of the color of these ions decreases each time, therefore the rate of disappearance of these ions increases.</p>	1

2.3.2	The increase in this rate is due to $Mn^{2+}$ ions formed that plays the role of a catalyst in this study and which is a product of the reaction (its concentration increases from one addition to another). The name of this phenomenon is the auto catalysis.	0.75
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### Second exercise(6pts)(GS)

Part of the Q	Answer	Mark
1.1	The result of the first experiment shows that the aqueous solution of A does not contain ions. The result of the second experiment shows that A can be an alcohol or an acid, because alcohols and acids react with sodium to give hydrogen gas and it is not an acid because it did not give ions in water. The result of the third experiment shows that A can be a primary or secondary alcohol because, by dehydrogenation, it gives a carbonyl compound which gives a yellow precipitate with 2,4-DNPH.	1.5
1.2	The carbon chain of A is saturated and does not contain a cycle, its molecular formula is thus of the form: $C_nH_{2n+1}OH$ .	0.5
2.1	According to the equation: $C_nH_{2n+1}OH + SOCl_2 \rightarrow C_nH_{2n+1}Cl + SO_2 + HCl$ we have : $n(A) = n(C_nH_{2n+1}Cl)$ ; $\frac{d \times V}{M(A)} = \frac{m(RCl)}{M(RCl)}$ . With: $M(A) = (14n + 18) \text{ g.mol}^{-1}$ ; $M(RCl) = (14n + 36.5) \text{ g.mol}^{-1}$ ; $d = 0.81 \text{ g.mL}^{-1}$ ; $V = 9.1 \text{ mL}$ and $m(RCl) = 9.2 \text{ g}$ . We obtain $n = 4$ , the molecular formula of A is $C_4H_9OH$ .	1
2.2	The possible condensed structural formulas of A are: $CH_3 - CH_2 - CH_2 - CH_2 - OH$ ; $CH_3 - CH_2 - CHOH - CH_3$ and $CH_3 - \underset{\begin{array}{c}   \\ CH_3 \end{array}}{CH} - CH_2 - OH$	0.75
3.1	The compound B is an aldehyde because it reacts with Fehling's solution, it comes from the dehydrogenation of a primary alcohol. This test thus does not make it possible to identify A, because there are two primary alcohols.	0.5
3.2	The carbon chain of A is not branched, it is thus 1-butanol.	0.25
3.3	The equations are: Reaction with sodium: $2 CH_3 - CH_2 - CH_2 - CH_2 - OH + 2 Na \rightarrow 2 CH_3 - CH_2 - CH_2 - CH_2 - ONa + H_2$ Dehydrogenation: $CH_3 - CH_2 - CH_2 - CH_2 - OH \rightarrow CH_3 - CH_2 - CH_2 - CHO + H_2$ Intramolecular dehydration: $CH_3 - CH_2 - CH_2 - CH_2 - OH \rightarrow CH_3 - CH_2 - CH = CH_2 + H_2O$	1.5