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

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 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 NH_3 and to prepare a buffer solution.

Given:

- This study is carried at 25 ºC.
- Molar volume of gas: $V_m = 24 \text{ L.mol}^{-1}$.
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Acid/base Couple	H_3O^+/ H_2O	NH_4^+ / NH_3	H_2O / HO^-
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 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 $[HO^-]$ with respect to C_b)
1.5- Determine the degree of conversion of ammonia in water.
1.6- Calculate the volume of 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 ($NH_4^+ + Cl^-$) of concentration $Ca = 6.0 \times 10^{-3} \text{ mol.L}^{-1}$ are mixed . 200 mL of a buffer solution of 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, 5.0×10^{-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)
Identification of an Organic Compound

The aim of this exercise is to identify a liquid organic compound A of unknown nature.

<u>Given</u> :

- Density of A : d = 0.81 $g.mL^{-1}$.
- Molar mass in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_O = 16$; $M_{Cl} = 35.5$

1- Identification of the Chemical Family of A

To identify A, some tests are carried out and the following results are noted :

- an aqueous solution of A does not conduct practically electric current.
- A reacts with sodium metal producing hydrogen gas.
- the catalytic dehydrogenation of A led to an organic compound B which gives a yellow precipitate with 2,4-DNPH.

1.1- Identify the chemical family of A based on the result of each of the three above tests.

1.2- Give the molecular formula of the compound A , of n carbon atoms , knowing that its carbon chain is saturated and non cyclic.

2- Determination of the molecular formula of A

A volume of 9.1 mL of A reacts with an excess $SOCl_2$ to give a mass of 9.2 g of an organic compound R – Cl according to the following equation:

$$A + SOCl_2 \rightarrow R-Cl + SO_2 + HCl$$

2.1- Show that the molecular formula of A is $C_4H_{10}O$.

2.2- Write the possible condensed structural formulas of A .

3- Identification of A

Compound B gives a brick- red precipitate when heated with Fehling's solution.

3.1- Verify if this test allows to identify A.

3.2- Give the name of A , knowing that its carbon chain is not branched.

3.3- Write the equations of the following reactions , using the condensed structural formulas of the organic compounds :

- action of A on sodium metal .
- catalytic dehydrogenation of A .
- intramolecular dehydration of A .

Third exercise (7 points)
Oxidation of Oxalic Acid

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

- Solution S_1 of oxalic acid $H_2C_2O_4$ of concentration $C_1 = 0.10$ mol.L^{-1}
- Solution S_2 of potassium dichromate ($2K^+ + Cr_2O_7^{2-}$)
- Solution S_3 of potassium permanganate ($K^+ + MnO_4^-$) of concentration $C_3 = 2.0\times10^{-2}$ mol.L^{-1}
- Concentrated sulfuric acid.

1- Oxidation of Oxalic Acid by Dichromate Ions

At a constant temperature, a volume V_1 of solution S_1, a volume V_2 of solution S_2 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:

$$Cr_2O_7^{2-} + 3\,H_2C_2O_4 + 8\,H_3O^+ \rightarrow 2\,Cr^{3+} + 6\,CO_2 + 15\,H_2O$$

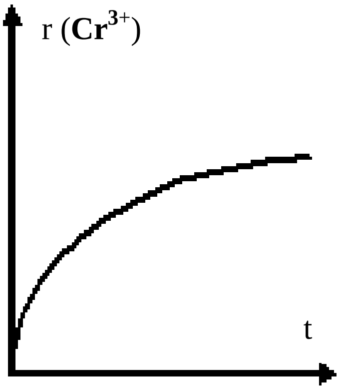
The variation of the concentration of dichromate ions versus time is followed with an appropriate method. The variation of the concentration of Cr^{3+} ions formed are deduced .
The results are grouped in the following table :

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

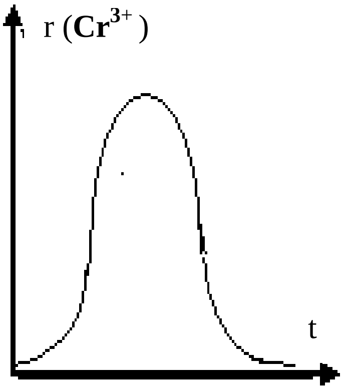
1.1- Plot the curve representing the variation of the concentration of Cr^{3+} ions versus time, $[Cr^{3+}] = f(t)$ in the interval of time: [0 – 300 s].
Take the following scale: 1 cm for 20s in abscissa and 1 cm for 1.0×10^{-3} mol.L^{-1} in ordinate.

1.2- Determine the rate of formation of Cr^{3+} ions at t = 100 s. Deduce the rate of the reaction at this instant.

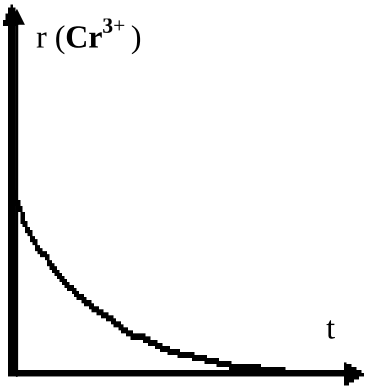
1.3- One of the three curves given below represents the variation of the rate of formation of Cr^{3+} ions versus time $r(Cr^{3+}) = g(t)$.
Choose, by justifying, the correct curve.



Curve a



Curve b



Curve c

2- Oxidation of Oxalic Acid by Permanganate Ions

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

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H_3O^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 14\ H_2O$$

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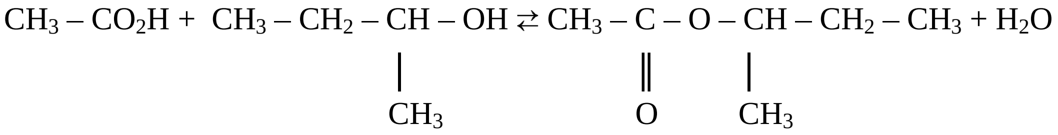
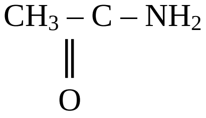
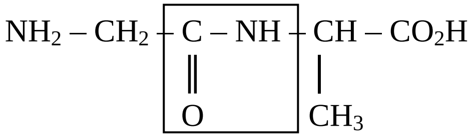
مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة : ساعتان	**الاسم:** **الرقم:**

First exercise (7 points)

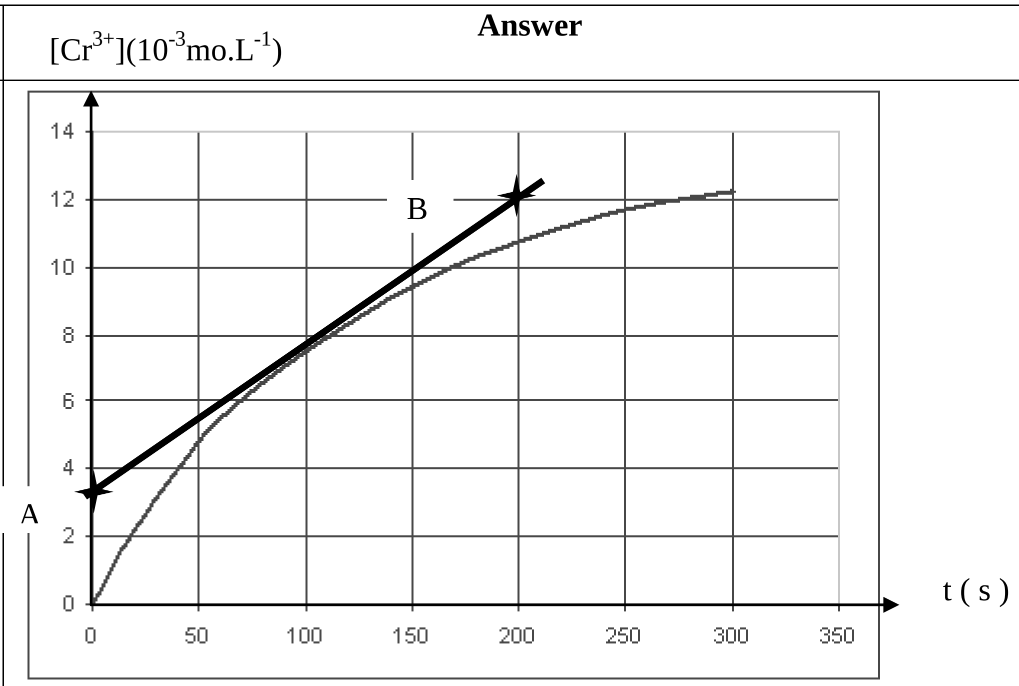
Part of the Q	Answer	Mark
1.1	Ammonia (NH_3) is a base because its dissolution in water leads to a medium of which pH = 10.6 > 7.	**0.5**
1.2	The equation of its reaction with water is: $NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + HO^-_{(aq)}$	**0.5**
1.3	The equilibrium constant of the equation of this reaction is: $K_R = \frac{[NH_4^+]\,[HO^-]}{[NH_3]}$ x $\frac{[H_3O^+]}{[H_3O^+]}$ Its value is: $\frac{10^{-14}}{10^{-9.2}} = 10^{-4.8}$ $K_R = 1.58\text{x}10^{-5}$.	**0.75**
1.4	Calculation of C_b: $10^{-4.8} = \frac{[HO^-]^2}{C_b - [HO^-]} = \frac{(10^{-3.4})^2}{C_b - 10^{-3.4}}$ $C_b = 0.01$ mol L^{-1}.	**0.5**
1.5	The coefficient of the dissociation α is given by: $\alpha = \frac{n(NH_3)\text{dissociated}}{n(NH_3)\text{introduced}} = \frac{[NH_4^+]}{C_b} = \frac{[HO^-]}{C_b} = \frac{10^{pH-14}}{C} = \frac{1.0\text{x}10^{-3,4}}{1.0\text{x}10^{-2}}$. $\alpha = 10^{-1,4} = 0.04$	**0.75**
1.6	The volume of ammonia gas: $V = n\text{x}V_m = C_b\text{x}V_{(S)}\text{x}V_m = 0.01\text{x}1\text{x}24 = 0.24$ 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: $NH_{3(aq)} + NH^+_{4(aq)} \rightleftharpoons NH^+_{4(aq)} + NH_{3(aq)}$	**0.5**
2.2	The initial quantities of NH_3 and NH_4^+ are conserved in the obtained solution : $pH = pKa + \log\frac{[NH_3]}{[NH_4^+]}$ permits to calculate the values of the two volumes. $9 = 9.2 + \log\frac{[NH_3]}{[NH_4^+]}$; $\log\frac{[NH_3]}{[NH_4^+]} = -0.2$ and $\frac{[NH_3]}{[NH_4^+]} = 0.63$. $\frac{n(NH_3)}{n(NH_4^+)} = \frac{V_1\times10^{-2}}{V_2\times6\times10^{-3}} = 0.63$ and $V_1 + V_2 = 200$ mL. So $V_1 = 55$ mL.	**1**
2.3.1	The equation of the reaction is: $H_3O^+_{(aq)} + NH_{3\,(aq)} \rightleftharpoons NH^+_{4\,(aq)} + H_2O_{(l)}$	**0.5**

2.3.2	$H_3O^+_{(aq)} + NH_{3\,(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + H_2O_{(l)}$ Initial state(n mol) 5.10^{-4} $5.5x10^{-4}$ $8.7x10^{-4}$ solvant Resulting solution -- $5.\,10^{-5}$ $13.7x10^{-4}$ solvant $PH = 9.20 + \log \dfrac{\frac{5x10^{-5}}{V(mixture)}}{\frac{13.7x10^{-4}}{V(mixture)}} = 7.76$	**1.5**

Second Exercice (6pts) (LS)

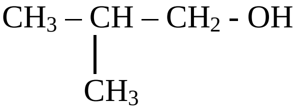
Part of the Q.	Answer	Mark
1	A : ethanoic acid ; B : 2-butanol et C : 2-aminoethanoic acid	0.75
2	B is the chiral compound since it contains an asymmetric carbon (the carbon number 2 of the hydrocarbon chain).	0.5
3.1	The equation of the reaction between A and B is  $CH_3-CO_2H + CH_3-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-OH \rightleftarrows CH_3-\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{CH_3}{\mid}}{CH}-CH_2-CH_3 + H_2O$ The name of the ester is: 1-methylpropyl ethanoate.	1
3.2	% of A esterified = $\frac{n(A)\,esterified}{n(A)\,initial}\times 100 = \frac{n(A)\,initial - n(A)remaining}{n(A)\,initial}\times 100 = \frac{0.2-0.08}{0.2}\times 100 =$ 60%.	0.75
4.1	The equation of this reaction: $CH_3-CO_2H + NH_3 \rightleftarrows CH_3-CO_2^- + NH_4^+$ 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 CH_3-CO_2H / $CH_3-CO_2^-$ and the base of the pair NH_4^+ / NH_3	0.5
4.3	The amide formed is  $CH_3-\underset{\underset{O}{\Vert}}{C}-NH_2$; 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 :  $NH_2-CH_2-\boxed{\underset{\underset{O}{\Vert}}{C}-NH}-\underset{\underset{CH_3}{\mid}}{CH}-CO_2H$	0.75

Third exercise (7 points)

Part of the Q	Answer	Mark
1.1		1
1.2	By definition: r(Cr^{3+}) = $\frac{d[Cr^{3+}]}{dt}$ at t = 100 s. Graphically, this rate represents the slope of the tangent to the curve $[Cr^{3+}]$ = f(t) at the point of abscissa t = 100 s. Consider on this tangent two points A and B whose co-ordinates are as follows: A (0; 3.2×10^{-3}) and B (200; 12.0×10^{-3}). According to the equation of the reaction, we can write: r($Cr^{3+})_{t=100}$ = $\frac{(12.0-3.2)\times10^{-3}}{200}$ = 4.4×10^{-5} mol.L^{-1}.s^{-1}. The rate of the reaction = r($Cr^{3+)}$ /2 = $2.2\text{x}10^{-5}$ mol.L^{-1}.s^{-1}.	1.5
1.3	According to the curve, r(Cr^{3+}) is maximum at t = 0, 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 **c.**	1
2.1	The disappearance of coloring is due to the disappearance of permanganate ions added .MnO_4^- is the limiting reactant.	0.5
2.2	The minimal volume that must be added is equal to a volume V_3 such as: $\frac{n(MnO_4^-)\,added}{2} = \frac{n(H_2C_2O_4)\,initial}{5}$ or $\frac{C_3\times V_3}{2} = \frac{C_1\times V_1}{5}$; Where $V_3 = \frac{2\times C_1\times V_1}{5\times C_3} = \frac{2\times0.1\times10}{5\times0.02}$ = 20 mL.	1.25
2.3.1	With each addition, n(MnO_4^-) 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.	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**

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) $g.mol^{-1}$; M(RCl) = (14n + 36.5) $g.mol^{-1}$; d = 0.81 $g.mL^{-1}$; V = 9.1 mL and m(RCl) = 9.2 g. We obtain n = 4, the molecular formula of A is C_4H_9OH.	**1**
2.2	The possible condensed strcutural formulas of A are: $CH_3 - CH_2 - CH_2 - CH_2 - OH$; $CH_3 - CH_2 - CHOH - CH_3$ and  $CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - CH_2 - OH$	**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**