وزارة التربية والتعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات الشهادة الثانوية العامة
فرع علوم الحياة

دورة سنة ٢٠٠٥ الاستثنائية

مسابقة في مادة الكيمياء
المدة: ساعتان

الاسم:
الرقم:

This Exam Includes **Three Exercises**. It Is Inscribed on Three Pages Numbered From **1** to **3.**
The Use of A Non-programmable Calculator Is Allowed

Answer the Three Following Exercises:

First Exercise (6 points)
From Milk to Dipeptide

Lactose, main carbohydrate of milk, of molecular formula $C_{12}H_{22}O_{11}$, degrades to give lactic acid of condensed structural formula: CH_3 – CH – C – OH.

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                  |      ||
                  OH     O
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Given:

- Molar mass of lactic acid: M = 90 $g.mol^{-1}$
- Milk is fresh when the concentration of lactic acid is lower than 1.8 $g.L^{-1}$
- Milk curdles when the concentration of lactic acid exceeds 5 $g.L^{-1}$

I- Study of the Condensed Structural Formula of Lactic Acid

Rewrite on the answer sheet the condensed structural formula of lactic acid.

1- Circle the two functional groups in the molecule of lactic acid and give their corresponding names.
2- Give the systematic name of lactic acid.
3- Justify the existence of two enantiomers of lactic acid. Represent these two enantiomers according to Cram's representation.

II- Titration of Lactic Acid in Milk

The lactic acid (weak acid noted as HA) in 20 mL of a milk is titrated with a sodium hydroxide solution of concentration $C_b = 5x10^{-2}$ $mol.L^{-1}$. Equivalence point is reached when the added volume of sodium hydroxide solution is V_{bE} = 11.9 mL.

1- Write the equation of the titration reaction.
2- Calculate the concentration of lactic acid in the studied milk.
3- Deduce if this milk can be considered as fresh or curdled milk.

III- From Lactic Acid to Dipeptide

An alcohol R – OH, when treated with hydrogen chloride, gives a chlorinated product R – Cl according to the equation of the following reaction:

$$R – OH + HCl \rightarrow R – Cl + H_2O$$

Compound R – Cl reacts with ammonia to give an amine according to the following equation:

$$R – Cl + 2\,NH_3 \rightarrow R – NH_2 + NH_4^+ + Cl^-$$

1- Referring to the above reactions, write the equations of the reactions that permit to pass from lactic acid to 2-amino propanoic acid.
2- Write the equation of the condensation reaction that permits to give the dipeptide from 2-amino propanoic acid.

Second Exercise (7 points)
An aldehyde: Ethanal

Ethanal is an organic compound highly used in chemical industry.
Ethanal is used in the preparation of ethanol, ethanoic acid, certain organic solvents, pharmaceutical products, … .
The melting and the boiling points of ethanal are respectively: θ_f = - 123 ºC and θ_b = 21 ºC.

I- Some Properties of Ethanal

1- Specify the physical state of ethanal at 18 ºC.
2- Indicate a chemical test to identify the reducing character of ethanal and give the expected corresponding observation.
3- Using condensed structural formulas, write the equations of the reactions that permit to prepare ethyl ethanoate from ethanal.

II- Kinetic of the Decomposition Reaction of Ethanal

In the gaseous phase, ethanal decomposes at high temperature T = 780 K, according to the equation of the following reaction: $C_2H_4O_{(g)} \rightarrow CH_{4\,(g)} + CO_{(g)}$
The kinetic study of this reaction is carried out by introducing n_0 mol of C_2H_4O in a closed evacuated container of constant volume V. The total pressure P_t that predominates in the container is measured in terms of time (t). This study gives the following results at T = 780 K.

t (min)	0	5	10	15	20	30	40	50	60	80	100
$P_t(10^3 Pa)$	24.0	28.0	30.8	33.0	34.8	37.4	38.8	40.0	41.0	42.4	43.2

1- Give the expression of the total number of moles of the gaseous mixture, n_t, in terms of n_0 and x, where x represents the number of moles of CH_4 formed at instant t.
2- Interpret the increase of the pressure P_t with time.
3- Calculate the total pressure, P_t , in the container at the end of the reaction.
4- Trace, on the graph paper, the curve that represents the variation of the pressure P_t in terms of time (t): $P_t = f(t)$.
Take the following scale: abscissa (1 cm for 10 min); ordinate (1 cm for 4×10^3 Pa).
5- Determine, graphically, the half-life of the reaction.

Third Exercise (7 points)
Dilution of a Weak Acid Solution

Chloroacetic acid is a weak acid which reacts with water according to the following equation:

$$CH_2ClCOOH + H_2O \rightleftarrows CH_2ClCOO^- + H_3O^+$$

I- <u>Study of a Solution of this Acid</u>

100 mL of a solution (S) are prepared by dissolving 0.01 mol of chloroacetic acid in distilled water.
The pH of this solution is 1.93.

1- Calculate the concentration C of chloroacetic acid in solution (S).
2- Establish the following relation: $\alpha = \frac{10^{-pH}}{C}$ where α represents the degree of dissociation of chloroacetic acid in water. Calculate α.
3- Show that the pK_a of the pair chloroacetic acid/chloroacetate ion is close to 2.81.

II- <u>Shape of the Curve of the Titration of (S) with a Strong Base</u>

A volume V = 20 mL of solution (S) is titrated with a sodium hydroxide solution of concentration $C_1 = 0.1$ mol.L^{-1} by using a pH-meter.

1- Calculate the volume V_{bE} of sodium hydroxide solution added to reach the equivalence point.
2- Find the coordinates of the half-equivalence point.
3- The pH of the obtained mixture is equal to:
7.78 at equivalence and 12.50 upon the addition of 40 ml of the basic solution.
Draw the shape of the curve pH = f(V_1), (V_1 is the volume of the basic solution added to carry out this titration and varies between 0 and 40 mL), using the coordinates of the four points previously found.
Take the following scale:
abscissa (1 cm for 2 mL); ordinate (1 cm for 1 unit of pH)

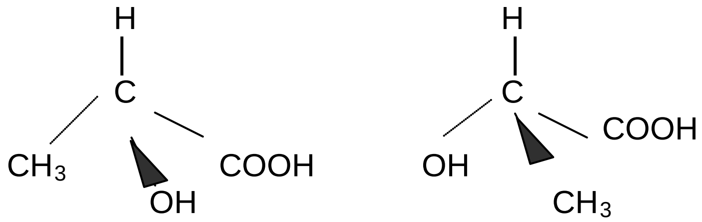
III- <u>Effect of dilution on solution (S)</u>

A sample of solution (S) is diluted 10 times to prepare a solution (S′). The measured pH of solution (S′) is 2.53.

1- Calculate the concentration C ′ of chloroacetic acid in solution (S′).
2- Deduce the effect of dilution of solution (S) on the degree of dissociation of chloroacetic acid in water.
3- A new titration is carried out, using a pH-meter, by adding progressively a sodium hydroxide solution of concentration 0.01 mol.L^{-1} into a beaker containing 20 ml of solution (S′). Justify that the obtained value of pH at the equivalence point, in this case, is between 7.00 and 7.78.

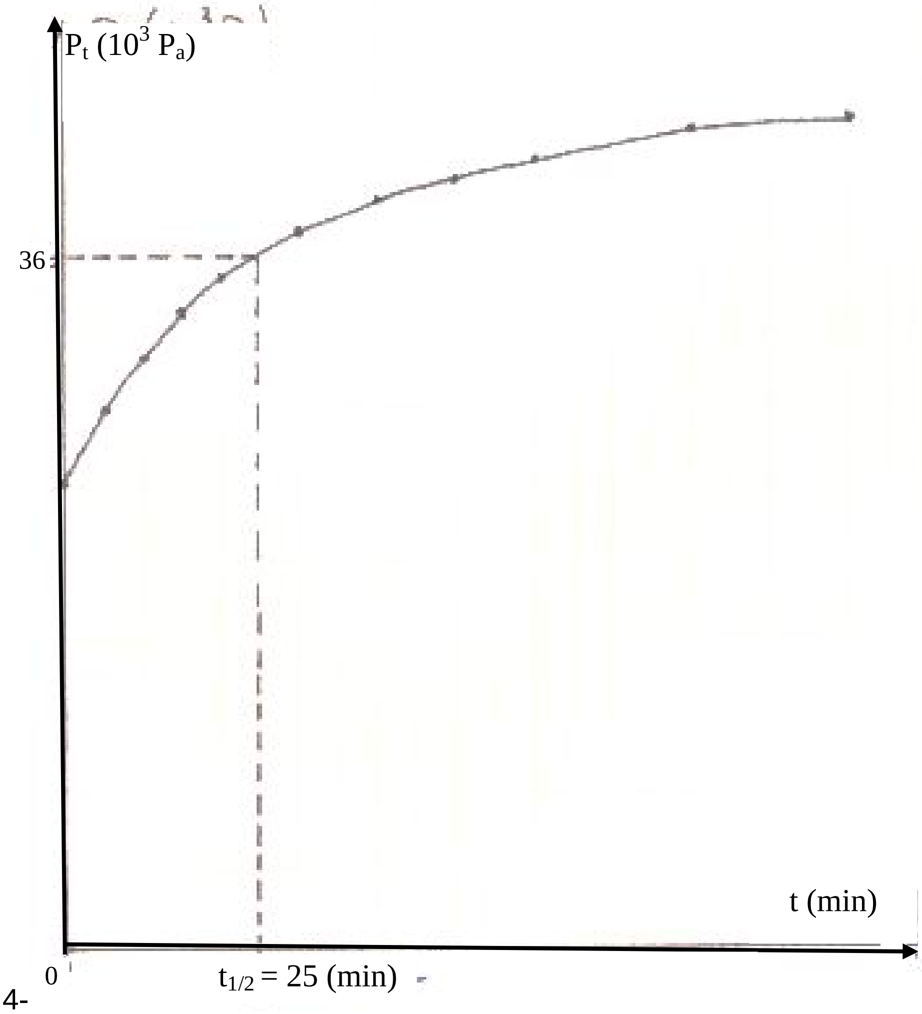
Marking Scheme **Life Sciences** **2^{nd} session 2005**

First exercise (6 points)
From milk to Dipeptide

Expected Answer	Mark	Comments
I- 1- $CH_3 - CH - C - OH$ (with $-OH$ on the CH boxed as Hydroxyl group; $C(=O)-OH$ boxed as Carboxyl group) Hydroxyl group / Carboxyl group	0.25x4	
2- The systematic name of lactic acid is 2-hydroxypropanoic acid.	0.5	
3- Carbon (2) in the carbon chain is attached to four different atoms or groups of atoms: H ; CH_3 ; OH ; and COOH. So carbon (2) is called asymmetric and there are two enanatiomers for lactic acid shown as follows:	0.5	
	0.5	
II- 1- The equation of the titration reaction is: $HA + OH^- \rightarrow H_2O + A^-$	0.5	
2- At equivalence, number of moles of lactic acid in 20 ml of milk is equal to the number of moles of the hydroxide ions in V_{bE}. Or $n_{mol} = C_{\text{in mol.L}^{-1}} \times V_{\text{in L of solution}}$ so: $C_aV_a = C_bV_{bE}$ $C_a = \frac{5 \times 10^{-2} \times 11.9}{20} = 2.925 \times 10^{-2}$ mol.L^{-1}	0.25x2	Explanation 0.25
3- The concentration of lactic acid in milk in g.L^{-1} is: $C = 2.925 \times 10^{-2} \times 90 = 2.63$ g.L^{-1}. Since $1.8 < 2.63 < 5$ so this milk is not fresh and does not curdle .	0.25x2	
III- 1- The equations of the reactions are : $CH_3 - CH(OH) - C(=O) - OH + HCl \rightarrow CH_3 - CH(Cl) - C(=O) - OH + H_2O$	0.5	
$CH_3 - CH(Cl) - C(=O) - OH + 2\ NH_3 \rightarrow CH_3 - CH(NH_2) - C(=O) - OH + NH_4^+ + Cl^-$	0.5	
2- The equation of the condensation reaction is : $CH_3 - CH(NH_2) - C(=O) - OH + H_2N - CH(CH_3) - C(=O) - OH \rightarrow CH_3 - CH(NH_2) - C(=O) - N(H) - CH(CH_3) - C(=O) - OH + H_2O$	1	

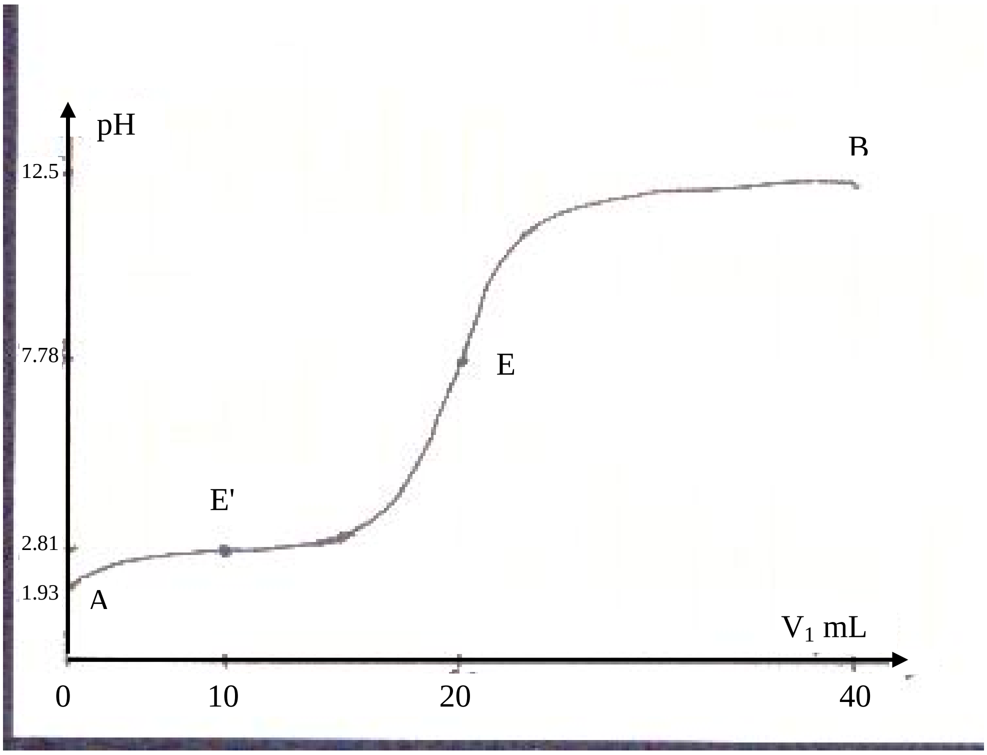
Second exercice (7 points)
An Aldehyde, Ethanal

Expected Answer	Mark	Comments
I- 1- At 18° C, ethanal is in the liquid state since its temperature is between the melting point – 123°C and the boiling point 21° C.	0.5	0 without explanation
2- Ethanal is a reducing agent Fehling solution test gives a red-brick precipitate with ethanal This identifies the reducing character of	0.25x2	Any other correct chemical test is

ethanal.		acceptable
3- The equations of the reactions that permit to pass from ethanal to ethyl ethanoate are:		
$CH_3-\underset{\underset{O}{\Vert}}{C}-H + \frac{1}{2}O_2 \rightarrow CH_3-\underset{\underset{O}{\Vert}}{C}-OH$	0.5	
$CH_3-\underset{\underset{O}{\Vert}}{C}-H + H_2 \rightarrow CH_3-CH_2-OH$	0.5	
$CH_3-\underset{\underset{O}{\Vert}}{C}-OH + CH_3-CH_2-OH \rightleftarrows CH_3-\underset{\underset{O}{\Vert}}{C}-O-CH_2-CH_3 + H_2O$	0.5	
II- 1- The equation of the reaction is : $C_2H_4O_{(g)} \rightarrow CH_{4\,(g)} + CO_{(g)}$ t = 0: n_0, 0, 0, $n_t = n_0$ t: $n_0 - x$, x, x, $n_t = n_0 + x$	1	
2- According to the equation of state of an ideal gas PV = nRT, P_t is directly proportional to n_t since T = constant and V= constant,	0.5	
so P_t increases as n_t increases with time	0.5	
3- At the end of the reaction, we have : $n_{t\infty} = 2n_0$ then $P_{t\infty} = 2P_0 = 2 \times 24 \times 10^3\ P_a = 48 \times 10^3\ P_a$		
 4-	1	
5- the half-life of the reaction is the time needed for half the number of moles of ethanal to be decomposed.	1.5	

$P_{t1/2} = \frac{3}{2}P_0 = 36x10^3$ Pa. Graphically : $t_{1/2}$ = 25 min.		

Third exercice (7 points)
Dilution of a solution of a weak Acid

Expected Answer	Mark	Comments
I- 1- The concentration of a solution is given by : $C = n_{\text{mol (soluté)}}/V_{\text{L (solution)}} = \frac{0.01}{0.1} = 0.1$ mol.L^{-1}.	0.5	
2- According to the equation of the reaction of the acid with water : $CH_2ClCOOH + H_2O \rightleftarrows CH_2ClCOO^- + H_3O^+$ t = 0 C 0 0 t $C(1-\alpha)$ $C\alpha$ $C\alpha$ We deduce : $[H_3O^+] = C\alpha$. so $\alpha = \frac{[H_3O^+]}{C} = \frac{10^{-pH}}{C} = 0.12$	1	
3- The constant K_a is shown by the expression : $K_a = \frac{[H_3O^+].[CH_2ClCOO^-]}{[CH_2ClCOOH]} = \frac{(10^{-1.93})^2}{0.1-10^{-1.93}} = 10^{-2.81}$ and $pK_a = 2.81$.	0.75	
II- 1- At equivalence: $n_{\text{chloroaceticc acid in 20 mL}} = n_{OH^-\text{ added}}$ So: $V_{bE} = \frac{C_A.V}{C_1} = \frac{0.1.x20}{0.1} = 20$ mL.	0.5	
The coordinates of the half-equivalence point E′ are : $pH = pK_a = 2.81$ and $V = \frac{V_{bE}}{2} = 10$ mL.	0.5	
2- The curve admits two inflection points. E (20 – 7.78) and E´ (10 – 2.81) and passes through the two points A (0 – 1.93) and B (40 – 12.5)  	1.5	
III-		

1- In dilution the number of moles of solute does not change $C' = C/10 = 0.01$ mol.L^{-1}. 2- $\alpha' = \frac{10^{-2,53}}{10^{-2}} = 0.295 > \alpha$. Dilution increases the degree of dissociation of chloroethanoic acid. 3- At equivalence, the major species are the same as the preceding titration. Na^+ is a spectator ion and CH_2ClCOO^- has basic character but with a lower concentration than before ; the pH remains greater than 7 but less than 7.78.	0.5 0.75 1	