

Entrance Exam 2008-2009

**CHEMISTRY** 

**Duration: 1 h** 

The Use of a Non-Programmable Calculator Is Allowed.

#### First Exercise (6points) Identification of an Ester

An ester E of molecular formula  $C_6H_{12}O_2$  derives from an alcohol A and an acid B. B is obtained starting with A. The carbon chain of A is opened and saturated.

- 1- Identify A, B and E.
- 2- Write the equation of the reaction allowing to obtain B from A.
- 3- Write the equation of the reaction giving E starting with A and B.
- 4- An organic compound C could be obtained during the passage from A to B. Suggest a test justifying the complete transformation of A to B.

#### Second Exercise (7 points) study of a Heterogeneous Chemical Equilibrium

Mercury II oxide decomposes by heating according to the following equation:

The aim of this exercise is to study this heterogeneous equilibrium at the temperature of 450 °C.

#### Given:

-Molar mass in g.mol<sup>-1</sup>: M (HgO) = 216.6

-Constant of ideal gas:  $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ 

#### 1-Study of the Equilibrium in an Empty Container

Introduce into a container of capacity 1L which is considered invariable with temperature, after having made the vacuum, at 25 °C, a mass *m* of pure mercuric oxide HgO.

Heat the container up to a constant temperature of 450 °C which is higher than the boiling point of mercury. An equilibrium is established (the reaction is very slow). The total pressure ( $P_{eq}$ ) at equilibrium is measured, it has a value  $P_{eq} = 3.9$  bar.

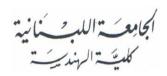
Represent by x the pressure of  $O_2$  at equilibrium.

- 1.1- Calculate the pressure x of oxygen gas.
- 1.2- Give, in terms of x the constant Kp of the equilibrium. Calculate Kp
- 1.3-Calculate the minimal value of m<sub>0</sub> which is necessary to be introduced into the container so that the equilibrium is established.

#### 2- Study of the Equilibrium in the Pressure of Oxygen gas.

The preceding experiment is modified as the following way:





After having made the vacuum in the container, introduce pure mercuric oxide at 25°C, introduce then an amount of oxygen gas such as its pressure is 0.385 bar at 25°C. The container is closed and carried at 450 °C.

- 2.1-Specify the effect of this modification on the position of equilibrium.
- 2.2-Establish the expression allowing to calculate the new total pressure obtained in terms of y the pressure of Hg at equilibrium.
- 2.3-Verify that the value of this pressure is P = 3.935 bar.

### Third Exercise (7 points) Buffer Solution

The purpose of this exercise is to prepare a solution of known pH.

#### Given:

Conjugate acid/base pair	$H_3O^+/H_2O$	CH <sub>3</sub> COOH/ CH <sub>3</sub> COO	H <sub>2</sub> O/HO	
pKa	0	4,8	14	

The two following solutions are available:

- -Solution  $S_1$  of sodium ethanoate (Na<sup>+</sup> + CH<sub>3</sub> COO<sup>-</sup>) of concentration  $C_1 = 0.02 \text{ mol.L}^{-1}$ ;
- -Solution  $S_2$  of hydrochloric acid ( $H_3O^+ + Cl^-$ ) of concentration  $C_2 = 0.05$  mol. $L^{-1}$ ; and the necessary glassware to carry out precise measurements.

It is required to prepare two buffer solutions:

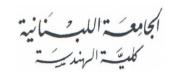
- Solution A of pH<sub>A</sub> = 5.1 by adding a volume  $V_1$  of  $S_1$  to a volume  $V_2$  of  $S_2$ .
- Solution B of pH<sub>B</sub> = 4.5 by adding a volume  $V_2'$  of  $S_2$  to a volume  $V_1'$  of  $S_1$ .

1-show, in each case, the following relation:

$$\frac{V_1}{V_2} = \frac{{V_1}'}{{V_2}'} = \frac{C_2}{C_1} \left( 1 + 10^{(pH - pKa)} \right)$$

- 2-Calculate the volume V<sub>1</sub> of S<sub>1</sub> which is needed to be added into a volume V<sub>2</sub> of S<sub>2</sub> to obtain 100 mL of A and the volume V<sub>2</sub>' of S<sub>2</sub> which is needed to be added into a volume V<sub>1</sub>' of S<sub>1</sub>. to obtain 250 mL of B.
- 3-A buffer solution of pH = 4.8 is prepared by mixing a volume x of  $S_1$  and a volume y of  $S_2$ . Find the relation between x and y in the two following cases:
- 3.1- Pour  $S_2$  in  $S_1$
- 3.2- Pour  $S_1$  in  $S_2$





### **Entrance Exam 2008-2009**

# Duration: 1 h Solution of Chemistry

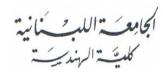
First Exercice (6 points) Identification of an Ester

Nº	Answer	Mark				
1	The acid coming from the mild oxidation of the alcohol, this alcohol is thus					
	primary. The acid and the alcohol contain in their molecules the same					
	number of carbon atoms. The ester is formed starting with A and B and					
	having in its molecule 6 atoms of carbon, each molecule A and B contains 3					
	carbon atoms. A is the 1-propanol of condensed structural formula					
	CH <sub>3</sub> – CH <sub>2</sub> – CH <sub>2</sub> OH. B is the propanoic acid of condensed structural					
	formula CH <sub>3</sub> – CH <sub>2</sub> – COOH					
2	It is a mild oxidation, the equation is then:	1				
	$CH_3 - CH_2 - CH_2OH + O_2 \rightarrow CH_3 - CH_2 - COOH + H_2O.$					
3	It is an esterification reaction:	1				
	$CH_3 - CH_2 - COOH + CH_3 - CH_2 - CH_2OH \rightleftharpoons CH_3 - CH_2 - COO - CH_2 -$					
	$CH_2 - CH_3 + H_2O$					
4	The organic compound which can be formed is the propanal. If the reaction	1				
	is complete there is not the compound C. the test is negative with DNPH					
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Second Exercise (7 points) study of a Heterogeneous Chemical Equilibrium

Nº	Answer		
1.1	The total pressure at equilibrium is: $P_{eq} = P_{O2} + P_{Hg} = x + 2 x = 3x = 3.9$ .	1	
	We draw: $x = 1.3$ bar.		
1.2	$Kp = P_{O2} \times (P_{Hg})^2 = x \times (2x)^2 = 4x^3 = 8.79.$	1	
1.3	So that equilibrium is established, it is necessary to have in the reacting	1,5	
	system all the components of the system.		
	$   n_0 = m_o/M_{\rm HgO} \ge n_{\rm O2  (eq)} = \frac{P({\rm O_2})V}{RT} = \frac{1.3 \times 10^5 \times 1.0 \times 10^{-3}}{8.314(273 + 450)} = 0.0216   {\rm mol.} $		
	The minimal value of the mass is: $m_0 = 0.0216 \times 216,6 \times 2 = 9.36$ g.		
2.1	Initially oxygen and mercuric oxide are introduced. To reach the Kp value, it		
	is necessary that a little less HgO dissociates.		



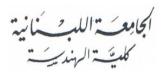


2.2							2
		2HgO(s)	2Hg(g)	$O_{2(g)}$	Ptotale		
	Initial state		<u>0</u>	0.385	0.385		
	Equilibrium		Y	$\frac{y}{2} + 0.385$	$\frac{3y}{2} + 0.385$		
	state			$\frac{-}{2}$ + 0.383	$\frac{-}{2}$ + 0.383		
	<u> </u>						
2.3	$Kp = (y)^2(\frac{y}{2} + 0.385) = 8.79.$						1
	With P = 3.935 bar we draw: $y = 2.367$ and Kp = 8.78. The value 3.935 is						
	checked						

### Third exercice (7 points) Buffer Solution

Nº	Answer						
1	When $S_1$ and $S_2$ are mixed a reaction will take place of equation:						
	$CH_3COO^- + H_3O^+ \Rightarrow CH_3COOH + H_2O$						
	Of which $Kr = 10^{4.8}$		_				
	To have a buffer solu			-			
	CH <sub>3</sub> COOH coexist i		se one to	the other and th	nat the H <sub>3</sub> O <sup>+</sup>		
	ions react completely	y al/facidl we draw	[hase]/[a	cidl — 10pH-pKa	$-10^{0.3} - 2$		
	pH = pKa + log[base]/[acid] we draw [base]/[acid] = $10^{pH-pKa} = 10^{0.3} = 2$ by adding S <sub>1</sub> to S <sub>2</sub> all H <sub>3</sub> O <sup>+</sup> are transformed to give CH <sub>3</sub> COOH and it is						
	necessary to add mor						
	,						
		CH <sub>3</sub> COO⁻	$H_3O^+$	CH <sub>3</sub> COOH	H <sub>2</sub> O		
	Initial state	$C_1V_1$	$C_2V_2$	0	Much		
	Equilibrium	$C_1V_1 - \frac{C_2V_2}{}$	0	$C_2V_2$	Much		
	state						
	W G						
	$\{C_1V_1 - C_2V_2\}/C_2V_2 = 10^{pH-pKa}$ On tire $\frac{V_1}{V_2} = \frac{C_2}{C_4}(1+10^{pH-pKa})$ .						
	V <sub>2</sub> C <sub>1</sub>						
2	$V_1 + V_2 = 100 \text{ mL}; \frac{V_1}{V_2} = \frac{0.05}{0.02} (1 + 10^{5.1 - 4.8}); V_1 = 75 \text{ mL} \text{ and } V_2 = 25 \text{ mL}$					2	
	$V_1 = 166.66 \text{ mL} \text{ and } V_2 = 83.33 \text{ mL}.$						
3	If we add the $S_2$ acid to the $S_1$ base that corresponds to half-equivalence.					1	
	$\frac{x}{1} = 2.5$						
	y						
	If we add the $S_1$ base to the $S_2$ acid that corresponds to the double of						





volume at equivalence.  $\frac{x}{y} = 5$ .

