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:

$$2\,HgO_{(s)} \rightleftharpoons 2\,Hg_{(g)} + O_{2\,(g)}$$

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

Given:
-Molar mass in $g.mol^{-1}$: M (HgO) = 216.6
-Constant of ideal gas: R = 8.314 $J.mol^{-1}.K^{-1}$

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_0 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_3COOH/ CH_3COO^-	H_2O/HO^-
pKa	0	4,8	14

The two following solutions are available:
-Solution S_1 of sodium ethanoate ($Na^+ + CH_3COO^-$) of concentration $C_1 = 0.02$ 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 $pH_A = 5.1$ by adding a volume V_1 of S_1 to a volume V_2 of S_2.
- Solution B of $pH_B = 4.5$ 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:

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

2-Calculate the volume V_1 of S_1 which is needed to be added into a volume V_2 of S_2 to obtain 100 mL of A and the volume V_2' of S_2 which is needed to be added into a volume V_1' of S_1. 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

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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 $CH_3 - CH_2 - CH_2OH$. B is the propanoic acid of condensed structural formula $CH_3 - CH_2 - COOH$	**3**
2	It is a mild oxidation, the equation is then: $CH_3 - CH_2 - CH_2OH + O_2 \rightarrow CH_3 - CH_2 - COOH + H_2O$.	**1**
3	It is an esterification reaction: $CH_3 - CH_2 - COOH + CH_3 - CH_2 - CH_2OH \rightleftharpoons CH_3 - CH_2 - COO - CH_2 - CH_2 - CH_3 + H_2O$	**1**
4	The organic compound which can be formed is the propanal. If the reaction is complete there is not the compound C. the test is negative with DNPH	**1**

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

Nº	Answer	Mark
1.1	The total pressure at equilibrium is: $P_{eq} = P_{O2} + P_{Hg} = x + 2x = 3x = 3.9$. We draw: $x = 1.3$ bar.	**1**
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 system all the components of the system. $n_0 = m_o/M_{HgO} \geq n_{O2\ (eq)} = \dfrac{P(O_2)V}{RT} = \dfrac{1,3\times10^5 \times 1.0\times10^{-3}}{8.314(273+450)} = 0.0216$ mol. The minimal value of the mass is: $m_0 = 0.0216 \times 216,6 \times 2 = 9.36$ g.	**1,5**
2.1	Initially oxygen and mercuric oxide are introduced. To reach the Kp value, it is necessary that a little less HgO dissociates.	**0,5**

2.2	<table><tr><td></td><td>$2HgO_{(s)}$</td><td>$2Hg_{(g)}$</td><td>$O_{2(g)}$</td><td>P_{totale}</td></tr><tr><td>Initial state</td><td>---</td><td>**0**</td><td>0.385</td><td>0.385</td></tr><tr><td>Equilibrium state</td><td>---</td><td>Y</td><td>$\frac{y}{2}+0.385$</td><td>$\frac{3y}{2}+0.385$</td></tr></table>	2
2.3	$Kp = (y)^2(\frac{y}{2} + 0.385) = 8.79$. With P = 3.935 bar we draw: $y = 2.367$ and Kp = 8.78. The value 3.935 is checked..	1

Third exercice (7 points) Buffer Solution

Nº	Answer	Mark
1	When S_1 and S_2 are mixed a reaction will take place of equation: $$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$ Of which $Kr = 10^{4.8} > 10^4$ the reaction is complete. To have a buffer solution, it is necessary that the two species CH_3COO^- and CH_3COOH coexist in proportions close one to the other and that the H_3O^+ ions react completely pH = pKa + log[base]/[acid] we draw [base]/[acid] = $10^{pH-pKa} = 10^{0.3} = 2$ by adding S_1 to S_2 all H_3O^+ are transformed to give CH_3COOH and it is necessary to add moreover CH_3COO^- such as: <table><tr><td></td><td>CH_3COO^-</td><td>H_3O^+</td><td>CH_3COOH</td><td>H_2O</td></tr><tr><td>Initial state</td><td>C_1V_1</td><td>C_2V_2</td><td>0</td><td>Much</td></tr><tr><td>Equilibrium state</td><td>$C_1V_1 - C_2V_2$</td><td>0</td><td>C_2V_2</td><td>Much</td></tr></table> $\{C_1V_1 - C_2V_2\}/ C_2V_2 = 10^{pH-pKa}$ On tire $\frac{V_1}{V_2} = \frac{C_2}{C_1}(1 + 10^{pH-pKa})$.	4
2	$V_1 + V_2 = 100$ mL; $\frac{V_1}{V_2} = \frac{0,05}{0,02}(1 + 10^{5,1-4,8})$; $V_1 = 75$ mL and $V_2 = 25$ mL $V'_1 = 166.66$ mL and $V'_2 = 83.33$ mL.	2
3	If we add the S_2 acid to the S_1 base that corresponds to half-equivalence. $\frac{x}{y} = 2.5$ If we add the S_1 base to the S_2 acid that corresponds to the double of	1

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