

**END OF SEMESTER "CHEMISTRY 2" EVALUATION (3h)**

No documents allowed. All answers must be justified

Gases shall be considered ideal

For all calculations:  $R = 8.314 \text{ J.mol}^{-1}\text{K}^{-1}$ ;  $760 \text{ torrs} = 1.00 \text{ atm} = 1.013 \text{ bar} = 101325 \text{ Pa}$ ;

$T_0 = 273 \text{ K} = 0^\circ\text{C}$

Several data are given at the end of the subject

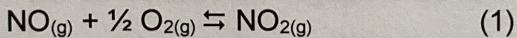
**Towards cleaner vehicles (40 pts)**

Increasingly drastic environmental legislations and regulations are encouraging car manufacturers to market more efficient and clean vehicles, particularly in terms of carbon dioxide  $\text{CO}_2$  and nitrogen oxides emissions. This subject explores different strategies which may contribute to this effort.

The three exercises are fully independent.

**Exercise I- Pollution control of combustion engine exhaust gases (14.5 points)**

In addition to  $\text{CO}_2$ , the combustion of fuel in an engine produces nitrogen oxides ( $\text{NO}_x$ ) which are made of  $\text{NO}$  and  $\text{NO}_2$ . These gases can have negative impacts on human health.  $\text{NO}_2$  is considered to be 4 times more toxic than  $\text{NO}$  and 10 times more toxic than carbon monoxide,  $\text{CO}$ . These gases also have negative impacts on the environment as they can lead to the formation of nitric acid and ozone in the presence of heat and light. Automobile manufacturers have therefore developed systems to remove nitrogen oxides from exhaust gases.

**I.1- NO- $\text{NO}_2$  equilibrium**

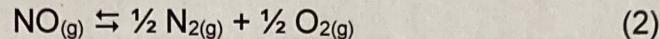
- Calculate the variance of this equilibrium starting from an initial stoichiometric mixture of  $\text{NO}$  and  $\text{O}_2$  then show that the calculated value is consistent with a system of equations that you will indicate.
- Assuming that the initial state is a stoichiometric mixture of  $\text{NO}$  and  $\text{O}_2$ , express the equilibrium constant  $K^0(T)$  as a function of the total pressure  $p_t$  and the conversion of  $\text{NO}$  (noted  $\alpha$ ), defined as the ratio of the number of moles of  $\text{NO}$  that reacts to the initial number of moles of  $\text{NO}$ .
- Using the thermodynamic data provided in the appendix, express  $K^0(T)$  as a function of  $T$  in the form of  $\ln(K^0(T)) = -\frac{A}{T} + B$ .
- The temperature of the exhaust gas leaving the engine is estimated to be  $800^\circ\text{C}$ . Show that  $\alpha = 0.05 \pm 0.01$  at  $800^\circ\text{C}$  under a total pressure  $p_t$  of 1 bar. Deduce therefrom the molar and the volumetric compositions of the gaseous mixture of  $\text{NO}_x$  (assumed ideal) under these conditions.
- What must be the temperature to reach  $\alpha = 0.95$ ? Would it be possible to predict without calculation how the composition of the gaseous mixture of  $\text{NO}_x$  would change with the temperature? Justify your answer.
- How would a change in the total pressure influence this equilibrium? Justify your answer.

In fact, the exhaust gas is made of almost 99%  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and less than 1% of  $\text{NO}_x$ .  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are considered as inert gases in the reaction.

- What would be the influence of the addition of a mixture of inert gases at constant temperature and total pressure on the reaction that consumes  $\text{NO}_{(g)}$ ?

## I.2- Decomposition of nitrogen oxides NO<sub>x</sub>

NO<sub>(g)</sub> may decompose into di-nitrogen and di-oxygen according to the following reaction:



Let's consider a gas mixture initially composed of 70.00 mol N<sub>2</sub>, 9.00 mol O<sub>2</sub> and 1.00 mol NO, placed at a temperature of 800 ° C under an overall pressure p<sub>t</sub> of 1.00 bar.

8. Assuming that only reaction (2) takes place, would the composition of the mixture change and if so, in what direction? (final state composition is not asked).

In reality, reaction (2) is very slow and requires the use of a catalyst to occur significantly at a temperature below 900 ° C. As an alternative, a NO<sub>x</sub> depollution technology, called SCR (Selective Catalytic Reduction), consists in the injection of an aqueous solution of urea NH<sub>2</sub>CONH<sub>2(l)</sub> at the engine outlet, followed by the catalytic treatment of the exhaust gas by contact with a metal catalyst (based on vanadium oxide, iron or copper) as shown in Figure 1. In a first step, urea decomposes above 175°C in the presence of water into ammonia NH<sub>3</sub> according to reaction (3) below. In a second step, ammoniac can react with nitrogen oxides NO<sub>x</sub> to produce di-nitrogen and water according to reaction (4) below.

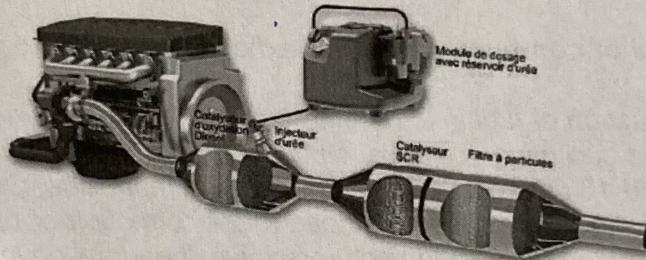
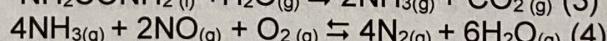
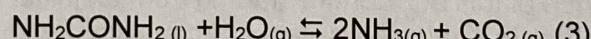


Figure 1- Exhaust gas treatment system in Diesel-fueled engines

In the presence of di-oxygen ("standard" SCR process), the following equilibria are involved:



9. Calculate the equilibrium constant of each equilibrium (3) and (4) at 800°C. What do you conclude?
10. Do you see advantages of this technology as compared to the treatment based on equilibrium (2)?

## Exercise II- « Bio-ethanol » as a fuel (17.25 points)

This exercise aims at comparing the amount of energy produced by different chemical processes that consume bioethanol as a fuel. Part II.1 involves a redox process to produce electrical energy, while part II.2 concerns a combustion reaction (thermal energy). Bioethanol is considered as a "clean" fuel because it is produced from renewable biomass resources (energy crops) or waste, whose production consumes carbon dioxide CO<sub>2</sub>, thereby compensating for the CO<sub>2</sub> emitted by the combustion of the fuel in cars engines, making the carbon balance close to neutral.

### II.1- Ethanol – dioxygen fuel cell

A fuel cell is set up in which liquid ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) is dissolved in water. Ethanol is converted into CO<sub>2(g)</sub> at one of the electrodes, while O<sub>2(g)</sub> is transformed into water at the other electrode. The electrolyte is an aqueous solution of sulfuric acid, and the electrodes are made of platinum. The two electrodes are separated by a porous membrane, which will be assumed to be impermeable to ethanol but permeable to sulfuric acid. The diagram of this cell, to be completed, is provided in the appendix.

1. Complete the description of the fuel cell given in the appendix by indicating:
  - The respective position of the anode and the cathode. Justify.
  - The polarity of each electrode.
  - The reactants and products present at each electrode.
  - The direction of the circulation of the electrons in the electrical circuit.
2. Give the literal expression of the potential of each electrode, specifying the numerical values of the standard potentials and the number of moles of electrons exchanged.
3. Give the overall reaction taking place in the fuel cell when it delivers a current.
4. Calculate the electromotive force of the cell (emf), noted  $\varepsilon$ , assuming that the reaction occurs under standard conditions. Deduce the electrical energy produced by the consumption of one mole of ethanol in these conditions.

One of the current technical limitations is the incomplete oxidation of ethanol into ethanoic acid ( $\text{CH}_3\text{COOH}$ ).

5. Give the corresponding half-reaction.
6. Give the overall redox reaction occurring in the fuel cell thereby obtained.
7. Calculate the electrical energy produced by the consumption of one mole of ethanol in this cell, assuming the reaction occurs under standard conditions. Conclusion?

## II.2- Combustion of ethanol – dioxygen mixture

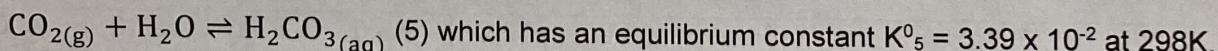
### *Part A: Evaluation of the thermal energy produced*

We want here to determine the amount of heat produced by the combustion of 1 mole of ethanol using an experimental protocol of calorimetry. The conditions of this experiment are as follows: 3.00 g of liquid ethanol are completely burned in an adiabatic calorimeter containing 1000 mL of water at an initial temperature  $T_i = 298 \text{ K}$ . Air is supplied to provide dioxygen in stoichiometric proportion with respect to the ethanol. At the end of the experiment, the calorimeter and its contents are at a temperature  $T_f = 318 \text{ K}$ . It will be assumed that the reaction occurs under monobaric conditions. The heat capacity of the calorimeter will be considered negligible as compared to that of the chemical system.

1. Write the balance equation for the reaction of combustion of ethanol, with the formation of  $\text{CO}_{2(g)}$  and liquid water. The reaction of combustion will be considered quantitative (i.e. total).
2. Establish a material balance of the contents of the calorimeter before and after the reaction.
3. Calculate the experimental value of the standard molar enthalpy of the combustion reaction of ethanol (liquid) at 298K.

### *Part B: Effect of the partial dissolution of $\text{CO}_{2(g)}$ produced from ethanol combustion during the calorimetric experiment.*

At the contact with a volume of liquid water  $\text{CO}_{2(g)}$  is partitioned between the gaseous phase in the form of  $\text{CO}_{2(g)}$  and the aqueous phase in the form of  $\text{CO}_{2(aq)}$ , which can then be hydrated into carbonic acid  $\text{H}_2\text{CO}_{3(aq)}$ . The overall phenomenon may be described by a single equilibrium according to the following equilibrium (5):



Carbonic acid is a diacid with two weak acidities in water. Related pKa values are given in the appendix.

1. Give the 4 equilibria which have to be considered in this exercise, along with the literal expression of their respective equilibrium constant.
2. Draw the diagram of predominance of the species  $\text{H}_2\text{CO}_{3(aq)}$ ,  $\text{HCO}_{3^-}_{(aq)}$  et  $\text{CO}_{3^{2-}}_{(aq)}$  as a function of the pH of the aqueous solution.

3. Qualitatively, what is the effect of the dissolution of carbon dioxide on the pH of the initially neutral water? Which one of the following species is then in minority:  $\text{H}_2\text{CO}_{3(\text{aq})}$ ,  $\text{HCO}_{3^{-}(\text{aq})}$  or  $\text{CO}_{3^{2-}(\text{aq})}$ ?

We are now willing to model the effect of the production of  $\text{CO}_{2(\text{g})}$  in the calorimeter, on the acid-base properties of the liquid phase. A specific experiment is carried out under the following conditions: an initial quantity of  $n_0 = 15.0 \times 10^{-2}$  mol of  $\text{CO}_{2(\text{g})}$  is contacted with a volume  $V_{\text{eau}} = 1,00\text{L}$  of initially neutral water (pH 7) in a calorimeter having a total volume  $V_t$  ( $V_t > V_{\text{eau}}$ ). The temperature is considered to be constant and equal to 298K. The possible evaporation of the water will be neglected. The pressure of  $\text{CO}_{2(\text{g})}$  is measured:  $P_{\text{CO}_2} = 1.00\text{bar}$ .

4. Calculate the final pH of the aqueous solution. Some relevant approximations are possible which have to be verified *a posteriori*.
5. Calculate the proportion of the initial  $\text{CO}_{2(\text{g})}$  which has been transferred into the aqueous solution at the final state of equilibrium.
6. What is then the volume occupied by the gas assuming that  $P_{\text{CO}_2}$  remains equal to 1.00 bar?

### Exercise III- Water-methanol binary system (8.25 points)

Methanol ( $\text{CH}_3\text{OH}$ ) is another alcohol which is also used to make fuel cells with di-oxygen. These batteries are generally not very powerful but have a long autonomy. During cell operation, liquid methanol oxidizes in the presence of liquid water. This exercise considers the isobaric L/V phase equilibria of the water-methanol binary system.

In this exercise, the total pressure is supposed constant and equal to 760 torrs.

1. Assuming water - methanol liquid solutions are ideal solutions, establish the expression of the molar composition of the liquid phase  $x_{\text{methanol}}$  and vapor phase  $y_{\text{methanol}}$  in equilibrium, according to the data provided in the table below. Calculate  $x_{\text{methanol}}$  and  $y_{\text{methanol}}$  at a temperature  $T = 73^{\circ}\text{C}$ .
2. Plot the water - methanol isobaric diagram between 60 and  $110^{\circ}\text{C}$  on the graph sheet provided in the appendix. Indicate the name of the curves and the nature of the phases in each domain.
3. A solution is prepared by mixing 101 mL of liquid methanol and 15 mL of liquid water. The temperature of this mixture is gradually increased until the formation of first bubbles of vapor is observed at a temperature  $\theta = 67^{\circ}\text{C}$ . Comment on this result.
4. A second mixture having a molar fraction of methanol equal to 0.600 is placed in a distillation device. The total mass of the mixture is equal to 100g.

- 4a) Make a scheme of the distillation device, specifying the name of each element.

Using the isobaric L/V equilibrium phase diagram plotted at question III-2 above, indicate:

- 4b) The temperature at which this mixture will start boiling  
 4c) The molar composition of the first bubbles of vapor  
 4d) Assuming the distillation process is complete with no loss of any constituent, indicate the nature and mass of the products recovered in the distillate and in the boiler at the end of the distillation.

### Water-Methanol binary system supposed ideal

T ( $^{\circ}\text{C}$ )	64.5	67.0	73.0	83.0	93.0	97.0	100
P*vap water (Torr)	192	213	273	407	592	683	760
P*vap methanol (Torr)	760	833	1034	1459	2019	2287	2505
$x_{\text{methanol}}$ (molar fraction)	1.000	0.882		0.336	0.118	0.048	0.000
$y_{\text{methanol}}$ (molar fraction)	1.000	0.967		0.645	0.313	0.144	0.000