

**« CHIMIE 2 »
Test n°2 –(1h30)**

*No document allowed – only TI30 type calculators are authorized
The 3 exercises can be solved independently. All answers should be justified.
The schedule of mark is indicative.*

Data to be used for computations : : $R=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $T_{0^\circ\text{C}} = 273 \text{ K}$;
 $1 \text{ atm} = 760 \text{ Torr} = 101325 \text{ Pa} = 1.013 \text{ bar}$. All gases are considered as ideal.

Exercise 1 - Homogeneous equilibrium: Dissociation of phosgene (10.5 pts)

Compound	$\Delta_f H_{(298\text{K})}^0$ (kJ.mol ⁻¹)	S_f^0 (298K) (J.mol ⁻¹ K ⁻¹)	$\overline{C_p}$ (J.mol ⁻¹ K ⁻¹)
COCl _{2(g)}	-220.1	283.8	57.0
CO _(g)	-110.5	197.7	29.1
Cl _{2(g)}	0	223.1	33.9

In gaseous phase, phosgene COCl₂ can dissociate into carbon monoxide (CO) and chlorine (Cl₂).

1. Write the corresponding equilibrium.

A] Lecture questions.

Let's consider as the chemical system a mixture of the 3 compounds, initially at equilibrium at 25°C.

2. How would the reaction evolve if:

- Temperature was increased, at constant pressure? Qualify.
- Volume was decreased, at constant temperature? Qualify.

3. Give the literal expression of the change in enthalpy $\Delta_r H_T^0$ and the change in entropy $\Delta_r S_T^0$ of dissociation of phosgene, as a function of the respective values at 25 °C and the heat capacities at constant pressure.

4. Show that on a given range of temperature lying between 25 °C and 427 °C, the previous expressions can be approximated to the values calculated at 25 °C. These approximations will be used in the following parts of the exercise.

B] Study of the equilibrium at $\theta_1 = 400$ °C.

5. Calculate $K_{p(\theta_1)}$ (in bars, to within 10⁻³) at $\theta_1 = 400^\circ\text{C}$.

6. Starting from phosgene only, express the dissociation degree in phosgene (α) as a function of the equilibrium constant K_P and the total pressure P_T . Calculate the value, at 400 °C and with $P_T = 1 \text{ bar}$.

7. In the experimental conditions of question 6, give the literal expression for the variance (number of degrees of freedom), define each parameter and calculate the value.

8. With defining the intensive variables of the equilibrium, show that the value is coherent with a set of equations linking all these variables.

9. Give the condition on the total pressure P_T such as the dissociation degree α is lower than 0.25.

C] Study of the equilibrium at $\theta_1 = 400\text{ }^\circ\text{C}$ in the presence of air.

In this experiment, phosgene was introduced in a container which volume is adjustable, and where some air was left. The chemical system is heated up to $\theta_1 = 400\text{ }^\circ\text{C}$, and the volume is adjusted such that $P_T = 1\text{ bar}$. We suppose that only the dissociation reaction can take place in these conditions.

10. How does the presence of air impact the dissociation degree in phosgene (noted α')? Qualify your answer.

11. Calculate α' in the specific case for which the amount of air left in the container is equal to the initial amount of phosgene that was introduced. Give the composition of the gaseous mixture at equilibrium.

Data : air will be considered as made of 80 mol.% of N_2 and 20 mol.% of O_2 .

Exercise 2 - Decomposition of BaO_2 . (4.5 points)

Let's consider the following equilibrium: $2\text{BaO}_{2(s)} \leftrightarrow 2\text{BaO}_{(s)} + \text{O}_{2(gaz)}$

At $\theta = 737\text{ }^\circ\text{C}$, when the equilibrium is attained, the measured pressure of O_2 which applies above the two non-miscible barium oxides is 0.186 bar.

1. Give the literal expression for the variance, define each parameter and calculate the value. Conclusion?

2. In a container where air was totally removed and with constant volume equal to 2 L, 9g of BaO_2 are introduced.

Give the composition of the system at equilibrium.

3. What would happen if, in the container was introduced some O_2 ? Some BaO ?

Data: Molecular weight: (in g/mol) Ba = 137.3 O = 16.0

Exercise 3 - pH of a mixture of a weak acid and a weak base (5 pts)

1. Calculate the pH of a solution of acetic acid CH_3COOH , which initial concentration C_A is $0.1\text{ mol}\cdot\text{L}^{-1}$. Each hypothesis that you may consider needs to be qualified.

2. Calculate the pH of a solution of ammonia NH_3 , which initial concentration C_B is $0.1\text{ mol}\cdot\text{L}^{-1}$. Each hypothesis that you may consider needs to be qualified.

By analogy with the acidity constant K_A , we can use the basicity constant K_B , which characterizes the reaction between a weak base and water, leading, among other products, to the formation of OH^- .

3. One mixes one volume of the previous acidic solution with one volume of the previous basic solution.

a/ Write down the acid/base reaction and calculate the associated equilibrium constant K. Conclusion?

b/ Calculate the pH of the mixture, and determine the values for $[\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-]$ and $[\text{NH}_4^+]/[\text{NH}_3]$ when equilibrium is attained.

Data at 298K:

$$\text{p}K_A (\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4.75$$

$$\text{p}K_A (\text{NH}_4^+/\text{NH}_3) = 9.2$$

$$\text{Water self-ionization of water: } K_e = 10^{-14}\text{ mol}^2\cdot\text{L}^{-2}$$

$$\text{For a given acid/base couple : } K_A \cdot K_B = K_e$$