

## CHEMISTRY 2

Short test n° 2 Duration : 1h 30

No document. Only calculators as « Collège » type are authorised  
The four exercises are independant. The indicated notation may evolve.

**General data :**  $T_0 = 273 \text{ K}$  1 bar =  $10^5 \text{ Pa}$

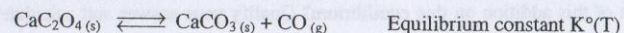
Gases are considered as mixtures of perfect gases.

Molar gas constant:  $R = 8.31 \times 10^{-2} \text{ bar.L.K}^{-1}.\text{mol}^{-1} = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$

### Exercise I : (5,5 points)

To study the dissociation of solid calcium oxalate  $\text{CaC}_2\text{O}_4(\text{s})$  into solid calcium carbonate  $\text{CaCO}_3(\text{s})$ , calcium oxalate  $\text{CaC}_2\text{O}_4(\text{s})$  is introduced into a closed flask, and air is evacuated under vacuum.

At high temperatures, calcium oxalate is known to dissociate into solid calcium carbonate and carbon monoxide according to the following equilibrium:



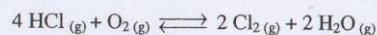
The table below gives the pressure measured in the system after equilibrium has been obtained at different temperatures:

T(K)	660	680	700	710
p (bar)	0.864	1.344	2.012	2.408

- $\text{CaC}_2\text{O}_4(\text{s})$  and  $\text{CaCO}_3(\text{s})$  being non miscible in the solid state, calculate the variance of this equilibrium. What can you deduce ?
- Plot  $\ln K^\circ(T)$  as a function of  $1/T$ . What can you deduce on the variation of the enthalpy of reaction as a function of  $T$  in this range of temperature? Calculate the enthalpy of reaction.
- At the temperature of 680 K, calculate the equilibrium constant  $K^\circ(680)$ , then  $\Delta_r G^\circ(680)$  and  $\Delta_r S^\circ(680)$  (to within 0.1 unit) of the reaction of dissociation of  $\text{CaC}_2\text{O}_4(\text{s})$ . Your calculations must be clearly explained.
- Calculate the minimum mass of calcium oxalate that has to be introduced in a 300 mL flask, initially under vacuum, to obtain the equilibrium at 660 K. ( $M_{\text{CaC}_2\text{O}_4} = 128 \text{ g.mol}^{-1}$ )

### Exercise II : Study of the equilibrium of Deacon (8 points)

Hydrogen chloride, HCl, is a by-product of chloration reactions. It can be recovered before being transformed into  $\text{Cl}_2(\text{g})$  according to a process known as the equilibrium of Deacon.



#### Thermodynamic data :

Substance	HCl (g)	O <sub>2</sub> (g)	H <sub>2</sub> O (g)	Cl <sub>2</sub> (g)
$\Delta_f H_{298}^\circ$ (kJ.mol <sup>-1</sup> )	-92.31	0	-241.8	0
$S_{298}^\circ$ (J.K <sup>-1</sup> .mol <sup>-1</sup> )	186.8	205.0	188.7	223.0

Pressure values have to be calculated to within 1 Pa. The numbers of moles have to be calculated to within 0.001 (round off the results according to usual rules).

The three questions are independant.

For each experiment, a table for the extent of the reaction has to be established.

- Predict and justify the influence on the equilibrium of :
  - an increase of temperature under constant pressure
  - an increase of pressure under constant temperature

2) In a first experiment, a mixture made of 0.40 mol of HCl, 0.10 mol of O<sub>2</sub> and 0.40 mol of N<sub>2</sub> (inert gas) in a flask of **variable volume**, maintained under **constant pressure**  $P = 1 \text{ bar}$  and at temperature  $T_1$ . At equilibrium, as the yield in  $\text{Cl}_2(\text{g})$  is 60%, calculate the numbers of moles of every constituent. Deduce the value of the equilibrium constant  $K^\circ(T_1)$ .

3) In a second experiment, 0.60 mol of HCl, 0.10 mol of O<sub>2</sub>, 0.15 mol of  $\text{Cl}_2(\text{g})$  and 0.20 mol of H<sub>2</sub>O are rapidly fed in a flask of **constant volume**, at the temperature of 350 K.

In those conditions, the total pressure is  $1.14 \times 10^5 \text{ Pa}$ . At this temperature, the reaction of Deacon is extremely slow and we can consider that the equilibrium is not reached. Then, temperature is increased up to 750 K. The equilibrium is established: then the partial pressure of dioxygène is 3% of the total pressure.

- Calculate the variance of the system at equilibrium
- Express the final pressure at equilibrium as a function of the initial pressure, of the temperatures and of any useful parameter. At the equilibrium, calculate the total pressure, and then the partial pressures of the constituents (in Pa, to within 1Pa). From this experiment, deduce the value of the equilibrium constant  $K^\circ(750)$ .
- Use the approximation of Ellingham ( $\Delta_r C_p$  considered as negligible) to compute an approached value of this constant  $K^\circ(750)$  thanks to thermodynamic data.
- 0.45 mol of argon (inert gas) is added at the equilibrium state obtained at 750 K. What is the effect of this addition on this equilibrium? Qualify your answer and calculate the total pressure.

### Exercise III : (3,5 points)

A plant that produces zinc rejects a purified gas (E) which molar composition is: 22% CO, 11% CO<sub>2</sub>, 1% H<sub>2</sub>, 66% N<sub>2</sub> at 298 K under 1 bar. This gas is burnt in a boiler. All the products of the combustion are in the gaseous state.

Calculate the maximal temperature reached by the whole of the gases if the combustion is total, isobaric, and adiabatic and assuming that :

- in the purified gas, only CO and H<sub>2</sub> are burnt,
- O<sub>2g</sub> is introduced at 298 K under 1 bar, in stoichiometric quantity, in the form of air (molar composition of air : 20% O<sub>2</sub>, 80% N<sub>2</sub>)

Data : Standard molar Enthalpies of combustion and heat capacities under constant pressure

	CO <sub>g</sub>	H <sub>2g</sub>	CO <sub>2g</sub>	H <sub>2</sub> O <sub>g</sub>	N <sub>2g</sub>
$\Delta_c \bar{H}_{298}^\circ$ (kJ.mol <sup>-1</sup> )	- 284	- 242			
$\bar{C}_p^\circ$ (J.K <sup>-1</sup> .mol <sup>-1</sup> )	$28 + 0.005 T$	$27.7 + 0.003 T$	$44 - 0.020 T$	$30 + 0.010 T$	$28 + 0.004 T$

### Exercise IV : (3 points)

1) Let's consider a solution of acetic acid CH<sub>3</sub>COOH of initial concentration  $C_0 = 10^{-2} \text{ mol.L}^{-1}$ .

Calculate its pH and the dissociation coefficient of the acid in those conditions.

2) The solubility of silver acetate in water is  $10.2 \text{ g.L}^{-1}$  at 25°C.

- Calculate the solubility constant  $K_s$ .
- What is the influence of the acidity on the solubility of silver acetate in water?
- Express the solubility of silver acetate as a function of the concentration in H<sub>3</sub>O<sup>+</sup> of the aqueous solution, of the acidity constant of acetic acid and of the solubility constant of silver acetate.

Data :  $\text{CH}_3\text{COOAg} = 166.9 \text{ g.mol}^{-1}$

Acidity constant of acetic acid:  $K_A = 1.75 \times 10^{-5}$

Autoprotolysis constant of water:  $K_e = 10^{-14}$ .