# CHEMISTRY TEST #2 (duration 1 h 30 min)

No document is allowed. Only non-programmable calculators are allowed.

Answers should be qualified. The schedule of mark is indicative.

Gases are supposed as ideal - $R=8.314\ J.mol^{-1}.K^{-1}$

## *Exercise I : Synthesis of hydrazine $N_2H_4$ (14 points)*

*The two parts are independent.*

Hydrazine ($N_2H_4$) is notably used as rocket fuel. It can be obtained from ammonia ($NH_3$) and dichlorine ($Cl_2$) as follows:

$$2\ NH_{3\ (g)} + Cl_{2\ (g)} \leftrightarrows N_2H_{4\ (g)} + 2\ HCl_{\ (g)} \qquad (1)$$

*Part 1 (9 points):*

1/ Is the equilibrium affected when:
- The pressure is increased at constant volume
- $NH_3$ is added at constant volume
- An inert gas is added at constant pressure

2/ Compute the variance at the equilibrium when starting from an initial mixture only constituted of ammonia and dichlorine in stoichiometric proportions. Prove that this value is consistent with a system of equations that you will establish.

3/ After giving a clear material balance in the form of a table of advancement, express the literal equation relating $K_{p1}$ -equilibrium constant related to pressures of (1)- to $r_1$ yield of hydrazine, when starting from an initial mixture of only ammonia and dichlorine in stoichiometric proportions.

4/ Compute $K_{p1}$ and $r_1$ at 298K.

5/ Calculate the partial pressure of each constituent at the equilibrium, the total pressure being equal to 0.1 bar.

*Part 2 (5 points):*

If the pressure is increased, the synthesized hydrazine can partly liquefy as follows:

$$N_2H_{4\ (g)} \leftrightarrows N_2H_{4\ (l)} \qquad (2)$$

6/ The boiling temperature (under 1 bar) of $N_2H_4$ is 387K and the corresponding heat of vaporization is 40500 $J.mol^{-1}$. Compute Pv -the saturated vapor pressure of $N_2H_4$ at 298K- assuming that the hypotheses used for integrating Clapeyron equation are valid.

7/ Compute the variance at the equilibrium when equilibria (1) and (2) simultaneously occur, starting from an initial mixture of only ammonia and dichlorine in stoichiometric proportions. Prove that this value is consistent with a system of equations that you will establish.

8/ Let x be the final pressure of $Cl_2$ at the equilibrium. Describe the equilibrium state by using pressure. Then deduce the literal expression relating x, $Kp_1$, $P_v$ and $P_T$- the total pressure at the equilibrium. Prove that this 3rd order equation admits x=0.1435 bar as a solution under $P_T$ = 1 bar and at 298K.

9/ It can be demonstrated that the yield of hydrazine $r_2$ can be written as: $r_2 = \frac{P_{HCl}}{P_{HCl} + 2P_{Cl_2}}$. Justify this equation and then compute $r_2$. Compare this value with the one for $r_1$.

**Data :**

| **Reactants** | **$\Delta_f G^0_{(298)}$ (kJ.mol$^{-1}$)** |
|---|---|
| $N_2H_4$ (g) | 159.3 |
| $NH_3$ (g) | -16.3 |
| $Cl_2$ (g) | 0 |
| HCl (g) | -95.3 |

***<u>Exercise II : Mixture of acids (6 points)</u>***

An aqueous acid solution is constituted of a mixture of formic acid ($HCOOH$ / $HCOO^-$) at a concentration C1, and acetic acid ($CH_3COOH$ / $CH_3COO^-$) at a concentration C2. The pH of this solution is equal to 3.

1- Write the equation of dissociation of each of these acids.
2- Calculate both dissociation coefficients ($\alpha_1$ and $\alpha_2$), the total concentration C1+C2 being equal to $10^{-2}$ mol.L$^{-1}$.
3- Calculate the respective concentrations C1 and C2 of these acids in the solution.
4- Calculate the pH of a solution only constituted of formic acid at C1. Calculate the dissociation coefficient $\alpha_1$' of this acid in such conditions.
5- Calculate the pH of a solution only constituted of acetic acid at C2. Calculate the dissociation coefficient $\alpha_2$' of this acid in such conditions.

**Data:**

$HCOOH/HCOO^-$ ($pK_{A1}$ = 3.75 at 25°C) ; $CH_3COOH/CH_3COO^-$ ($pK_{A2}$ = 4.76 at 25°C)
Ionic product of water : $K_e = 10^{-14}$ at 25°C