

CHEMISTRY TEST #2 (duration 1 h 30 min)

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

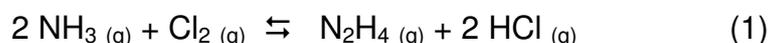
Answers should be qualified. The schedule of mark is indicative.

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

Exercise 1 : 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:

**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:



6/ The boiling temperature (under 1 bar) of N_2H_4 is 387K and the corresponding heat of vaporization is $40500 \text{ J}\cdot\text{mol}^{-1}$. Compute P_v -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 , K_{p1} , 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:

$r_2 = \frac{P_{\text{HCl}}}{P_{\text{HCl}} + 2P_{\text{Cl}_2}}$. Justify this equation and then compute r_2 . Compare this value with the one for r_1 .

Data :

Reactants	$\Delta_f G^0_{(298)} \text{ (kJ.mol}^{-1}\text{)}$
$\text{N}_2\text{H}_4 \text{ (g)}$	159.3
$\text{NH}_3 \text{ (g)}$	-16.3
$\text{Cl}_2 \text{ (g)}$	0
HCl (g)	-95.3

Exercise II : Mixture of acids (6 points)

An aqueous acid solution is constituted of a mixture of formic acid ($\text{HCOOH} / \text{HCOO}^-$) at a concentration C_1 , and acetic acid ($\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$) at a concentration C_2 . 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 (α_1 and α_2), the total concentration C_1+C_2 being equal to $10^{-2} \text{ mol.L}^{-1}$.
- 3- Calculate the respective concentrations C_1 and C_2 of these acids in the solution.
- 4- Calculate the pH of a solution only constituted of formic acid at C_1 . Calculate the dissociation coefficient α_1' of this acid in such conditions.
- 5- Calculate the pH of a solution only constituted of acetic acid at C_2 . Calculate the dissociation coefficient α_2' of this acid in such conditions.

Data:

$\text{HCOOH}/\text{HCOO}^-$ ($\text{pK}_{A1} = 3.75$ at 25°C) ; $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ ($\text{pK}_{A2} = 4.76$ at 25°C)
 Ionic product of water : $K_e = 10^{-14}$ at 25°C