IN DEPTH

37. Yield of esterification

In a flask of volume V, we introduce 57 mL of ethanoic acid and 58 mL of ethanol, 0.5 mL of concentrated sulfuric acid (H_2SO_4) and some grains of pumice stone are added, and the mixture is then boiled in a reflux heater for 30 minutes, a state of chemical equilibrium is established. The products obtained are treated in a suitable manner to separate the organic phase from the aqueous phase. At the end of the reaction, 64 mL of the ethyl ethanoate ester were collected.

Given :	Ethanoic acid	Ethanol	Ethyl ethanoate
Molar mass ($g.mol^{-1}$)	60	46.1	88.1
Density ($g.mL^{-1}$)	1.05	0.789	0.925

The equation of the esterification reaction :

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

Document 1

1. **Determination of the equilibrium constant K_c**

1.1. Calculate the initial number of moles of each of the ethanoic acid and ethanol and the number of moles of the ethyl ethanoate collected.

1.2. Deduce the yield of the esterification.

1.3. Determine the equilibrium constant K_c.

2. **Displacement of equilibrium**

In order to increase the amount of the ethyl ethanoate formed, a quantity of matter of 1 mol of ethanol is added at the same temperature to the mixture obtained at the equilibrium state above.

2.1. Specify in which direction the equilibrium displaces.

2.2. Determine the new composition in mol of the mixture obtained.

2.3. Compare the number of mole of the ester collected in the new mixture to the number of mole of the ester collected in the preceding mixture. Make a conclusion about the yield of the esterification.

2.4. Justify that the addition of few drops of sulfuric acid does not alter the value of the yield.

2.5. Propose a method to make the reaction quasi-complete.

38. Study of a state of equilibrium

Introducing an amount of 3 mol of iodine, 3 mol of hydrogen and 3 mol of HI into a container of volume 2 L previously empty of air and maintained at a constant temperature T. A reaction will take place leading to the following equilibrium of **document 1** :

$I_{2(g)} + H_{2(g)} \rightleftarrows 2HI_{(g)}$

The equilibrium constant $K_c = 49$ at the temperature of the experiment T.

Document 1

1. **Study of the initial mixture**
   1.1. Verify if the mixture initially introduced was already in equilibrium state.
   1.2. If the state of equilibrium has not yet reached, specify in what direction the reaction must proceed to reach the state of equilibrium.
2. **Study of the mixture at equilibrium**
   2.1. Recopy and complete the following table in terms of α the degree of dissociation of I_2:

Composition (mol)	I_2 (g)	H_2 (g)	HI (g)
Initial state	3	3	
Equilibrium state			

   2.2. Calculate α.
   2.3. Deduce the concentration of each component at equilibrium.
   2.4. The experiment shows that the degree of dissociation α' of the preceding equilibrium at a temperature T' < T is such that α' > α. Show that the forward reaction is exothermic.

39. Phosphorus pentachloride

Into an enclosure of volume V maintained at a constant temperature T = 250 °C, introduce a certain amount of phosphorus pentachloride $PC\ell_5$ equivalent to (a) mol. A reaction will take place leading to the following equilibrium of **document 1**:

$$PC\ell_5\,(g) \rightleftarrows PC\ell_3\,(g) + C\ell_2\,(g)$$

At equilibrium, 0.36 mol of $C\ell_2$, 0.3 mol of $PC\ell_5$ and $K_c = 4.3 \times 10^{-2}$ at T = 250 °C.

Document 1

1. **Determination of (a)**
   1.1. Determine the volume V of the enclosure.
   1.2. Using a table of numbers of mole in which the composition of the constituents of the equilibrium in the initial state and the equilibrium state appears, deduce the value of (a).
2. **Modification in theequilibrium state**

In another experiment carried out in the same volume V and at the same temperature T, a mixture (M) consisting of 0.5 mol of $PC\ell_5$, 0.5 mol of $PC\ell_3$ and 0.5 mol of $C\ell_2$ is introduced

41. Esterification reaction

The pure ethanoic acid CH_3-COOH reacts with pure methanol CH_3-OH to form the ester methyl ethanoate CH_3-COO-CH_3 and water according to a slow and limited esterification reaction represented by the following equation :

$$CH_3 - COOH + CH_3 - OH \rightleftarrows CH_3 - COO-CH_3 + H_2O$$

	Formula	M (g.mol^{-1})
Ethanoic acid	$CH_3 - COOH$	60
Methanol	$CH_3 - OH$	32

Document 1

- Concentrated sulfuric acid is a dehydrating substance if used in large mount in the esterification reaction.
- Concentrated sulfuric acid is a catalyst if used in a small amount in the esterification reaction.
- At 100 °C, $K_c = 4$.

Document 2

1. **Study of the reaction mixture**

30 g of ethanoic acid are mixed in a flask with 16 g of methanol and then the reaction mixture is heated for a time t at a temperature to 100 °C. A quantity x of the ester is formed.

1.1. Express the number of mole of each constituent at time t in terms of x.

1.2. An appropriate titration of the remaining acid shows that 0.25 mol of acid remains at time t. Verify if a chemical equilibrium state is attained at this instant of time.

1.3. Specify the effect of heating on the yield of the reaction.

2. **Experimental study**

A mixture of ethanoic acid and methanol when heated to 100 °C in the presence of a few drops of concentrated sulfuric acid, leads to the formation of 0.33 mol of ester after a few hours.

2.1. Show in this case that the chemical equilibrium is reached.

2.2. Deduce the coefficient of conversion of the acid at equilibrium.

2.3. Determine the yield Y of this esterification.

2.4. In the case where a large quantity of sulfuric acid is used. Indicate by justifying which of the following three proposals is correct :

a. $Y' < Y$ **b.** $Y' = Y$ **c.** $Y' > Y$

2.5. In the case where twice of the initial quantity of reactants is used, how will the yield of the esterification reaction be affected? Justify.

2.1. Specify in which direction the reaction will take place in the mixture (M).
2.2. Write the equation of the reaction which represents the new state of equilibrium.
2.3. Determine the constant K'_c corresponding to the new state of equilibrium.
2.4. Deduce the number of mole of each constituent at the new equilibrium state.

40. Synthesis of sulfur trioxide SO_3

Experiment 1 : In an empty enclosure of invariable volume V = 9 L maintained at a constant temperature T, a quantity equivalent to 0.4 mol of sulfur dioxide SO_2 gas and 0.2 mol of oxygen gas O_2 are introduced. After a certain time the following equilibrium is established **document 1 :**

$$2\,SO_{2(g)} + O_{2(g)} \rightleftarrows 2\,SO_{3(g)}$$

Document 1

1. **Study of the reaction mixture**

1.1. The amount of oxygen which has reacted at equilibrium is denoted by x. Express the number of moles of each constituent at equilibrium as a function of x.

1.2. Explain how the number of mole of the gas mixture has evolved from the initial state to the equilibrium state.

1.3. The number of moles of SO_2 at equilibrium is only 25 % of its initial value.

1.3.1. Show that x = 0.15 mol.

1.3.2. Calculate the amount of matter of each constituent at equilibrium.

1.4. Calculate the equilibrium constant K_c.

2. **Displacement of equilibrium**

The same experiment is repeated by modifying certain parameters, as indicated in documents 2 and 3.

Experiment 2 : The same experiment is repeated at a temperature T' > T, the concentration of SO_3 decreases.

Document 2

Experiment 3 : Experiment 1 is repeated by introducing at t = 0 an amount of 0.4 mol of SO_2, 0.2 mol of O_2 and 0.6 mol of SO_3. (The same volume V = 9 L is considered).

Document 3

2.1. Refer to **document 2**. Verify if the reaction is endothermic or exothermic in direction 1.

2.2. Referring to **document 3**. Specify in which direction the equilibrium should be displaced so that it will be re-established by performing the necessary calculation.

42. Dissociation of $N_2O_{4(g)}$

The aim of this exercise is to study the dissociation equation of N_2O_4 (colorless gas) into NO_2 (brown colored gas).

Given :

- Molar masses in $g.mol^{-1}$: $M_{(N_2O_4)} = 92$; $M_{(NO_2)} = 46$.
- α is the degree of dissociation of $N_2O_{4(g)}$.
- The extent of dissociation of the colorless gas $N_2O_{4(g)}$ into $NO_{2(g)}$ can be detected by the intensity of the brown color of NO_2 according to the following equation :

$$N_2O_{4(g)} \rightleftarrows 2\,NO_{2(g)}$$

1. Dissociation of $N_2O_{4(g)}$ at a temperature of 27° C :

In a closed bulb, we introduce a volume of N_2O_4 equivalent to 1.2 mol at a temperature of 27 °C (V and T are constant), the following equilibrium is established :

$$N_2O_{4(g)} \rightleftarrows 2\,NO_{2(g)}$$

The total number of moles of the mixture of gases at equilibrium $n_t = 1.32$ mol.

1.1. Express, in terms of α, the molar composition of the gaseous mixture at equilibrium.

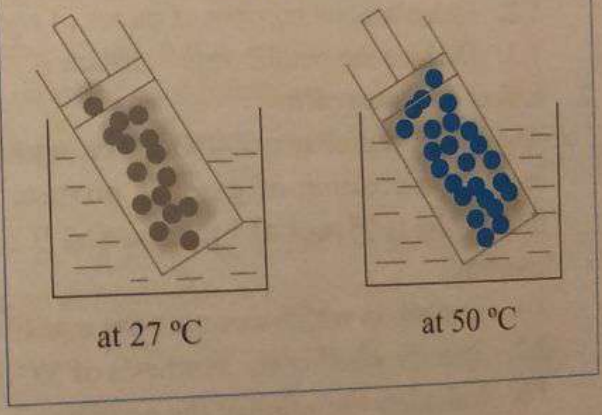
1.2. Show that $\alpha = 0.1$.

1.3. Write the expression of the equilibrium constant K_c.

2. Influence of temperature :

Each tube in **Document 1** contains a mixture of two gases $NO_{2(g)}$ and $N_2O_{4(g)}$. It is observed that the intensity of the red-brown color in the tube where the temperature is 50 °C is more than in the tube where the temperature is 27 °C.

Document 1



at 27 °C at 50 °C

2.1. Specify whether the dissociation reaction of N_2O_4 is exothermic or endothermic.

2.2. Choose the best answer. Justify

a. $K_{c\,(27°C)} = K_{c\,(50°C)}$ **b.** $K_{c\,(27°C)} < K_{c\,(50°C)}$ **c.** $K_{c\,(27°C)} > K_{c\,(50°C)}$.

2.3. Answer by true or false and correct the false answer :

a. The degree of dissociation α will decrease upon increasing the temperature from 27 °C to 50 °C.

b. Increasing the temperature will increases the yield of this reaction (if the forward reaction is endothermic).

3. Influence of concentration and catalyst at a constant temperature 27 °C :

3.1. The same experiment as in part 1 is repeated with only one change, we introduce a amount of 1 mol of NO_2 with 1.2 mol of N_2O_4. Choose by justifying the correct answer

a. $\alpha' < \alpha$ **b.** $\alpha' = \alpha$ **c.** $\alpha' > \alpha$.

3.2. To increase the yield of the reaction, a student suggests the following :

a. Eliminate NO_2 by an appropriate method.

b. Use an appropriate catalyst.

For each suggestion, indicate if it is correct or wrong. Justify.

43. Synthesis of Nitrosyl Bromide NOBr

The synthesis of nitrosyl bromide NOBr is schematized by the equation :

$$2\,NO_{(g)} + Br_{2\,(g)} \rightleftarrows 2\,NOBr_{(g)}$$

1. Equilibrium study :

In a bulb of volume 15 L, we introduce 0.6 mol of nitrogen monoxide NO and 0.3 mol of bromine gas Br_2 at a temperature $\Theta_1 = 700°C$.

At equilibrium the total number of moles of gaseous mixture is 0.85 mol.

1.1. Complete the following table :

	2 NO(g)	+	Br_2(g)	⇄	2 NOBr(g)
Initial state	0.6		0.3		0
Equilibrium state					2x

x represents the number of moles of NOBr obtained at equilibrium

1.2. Calculate the number of moles of each gas at equilibrium.

1.3. Deduce the equilibrium constant K_{c_1} at Θ_1.

2. Effect of temperature :

At a temperature $\Theta_2 = 800°C$, a new equilibrium state is established where the new molar composition of gaseous mixture is the following : 0.32 mol of nitrogen monoxide, 0.16 mol of bromine and 0.28 mol of nitrosyl bromide. (V and P are constant).

2.1. Explain in which direction the equilibrium is shifted

2.2. Specify whether the synthesis of NOBr is exothermic or endothermic.

2.3. Calculate the value of the equilibrium constant K_{c_2} at the temperature Θ_2.

3. Shifting Equilibria :

Under the same conditions of V and P, we consider a new mixture formed of 0.4 mol of NO ; 0.2 mol of Br_2 and 0.4 mol of NOBr at the temperature $\Theta_2 = 800\ °C$.

3.1. Choose from the following values the one corresponds to the quotient Q :

a. 71.7 **b.** 75 **c.** 57

Justify your answer.

3.2. Does the new mixture reach equilibrium? If not, Specify in which direction must be shifted to reach equilibrium?