UNIVERSITE LIBANAISE

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الجامعة اللبنانية
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**Entrance Exam 2010-2011** **Chemistry** **Time: 1 hour**

**July 04, 2010**

## First Exercise: The Ammonia (12 pts)

**Given**

- pKa of the conjugate acid//base pair $NH_4^+/NH_3$ = 9.2
- Ionic product of water, Kw = $1.0\times10^{-14}$
- Molar mass of ammonium chloride $NH_4Cl$ : M = 53.5 g.mol$^{-1}$

**1- Ammonia in an Aqueous Solution**

Ammonia in aqueous solution acts as a weak base.

1.1 Write the equation of the reaction of ammonia, $NH_3$, with water and express the equilibrium constant, Kc, of this reaction in terms of the acidity constant, Ka, of the considered acid/base pair and the ionic product of water, Kw.

1.2 Calculate the pH of an ammonia solution of concentration $1.00\times10^{-2}$ mol.L$^{-1}$.

**2 - Buffer Solution of Ammonia**

2.1 Write the equation of the reaction of ammonium ion with water.

2.2 Calculate the value of the ratio of concentrations $[NH_3]/[NH_4^+]$ in the buffered mixture when the pH is equal to 10.0.

2.3 Determine the mass of ammonium chloride, $NH_4Cl$, that will be dissolved, without notable variation of volume, in one liter of 2.00 mol.L$^{-1}$ ammonia solution to prepare a buffer solution of pH = 10.0.

2.4 The buffer solution thus prepared is used to carry out a titration at a controlled value of pH, close to 10. The beaker of titration contains initially 80.0 mL of the preceding buffer solution and the sample to be titrated. At the equivalence, the total volume in the beaker is 100 mL. The quantity of acid that reacts with ammonia is then $2.0\times10^{-3}$ mol of $H_3O^+$ ions.

2.4.1 Write the equation of the reaction of $H_3O^+$ ions with the buffer solution and show that it is practically complete.

2.4.2 Determine then the concentrations of NH3 and $NH_4^+$ at the equivalence point.

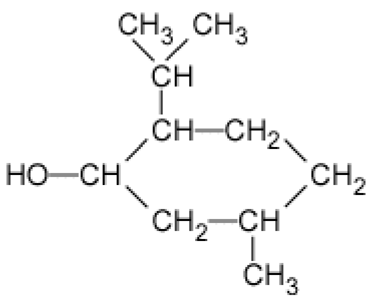
2.4.3 Calculate, at the equivalence, the new value of the pH. Comment the result while revealing the role of the buffer solution.

## Second Exercise: Kinetics of the Synthesis Reaction of Peppermint (8 pts)

Peppermint, calming, digestive … is well-known for its benefits since centuries. Used in perfumery, its essential oil contains an odorous ester: the menthyl ethanoate which is can be synthesized in the laboratory, starting with menthol and a carboxylic acid.

## 1- Preliminary Study

The condensed structural formula of menthol is denoted R-OH in this exercise and is given below:

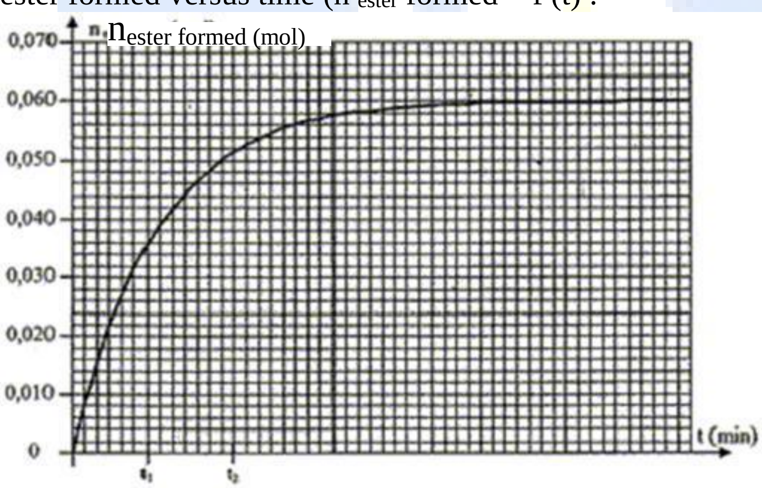



1.1- Specify the chemical family to which menthol belongs and indicate its class.
1.2- Write the condensed structural formula and give the name of the carboxylic acid which permits to syntheses menthyl ethanoate by reaction with menthol.
1.3- Using condensed structural formulas (simplified formula for menthol), write the equation of the synthesis reaction of the ester.
*The equilibrium constant K related to the equation of the above reaction is equal to 2.3 at 70°C.*

## 2- Synthesis of Menthyle Ethanoate

**Experimental Procedure of Experiment n°1**:

In order to synthesis menthyl ethanoate, 0.10 mol the above carboxylic acid, 0.10 mol of menthol, and a few drops of concentrated sulfuric acid are introduced into an Erlenmeyer flask immersed in ice. The mixture is equally distributed in 10 test tubes and an air condenser is adjusted to each tube. The 10 tubes are simultaneously plunged in a bath maintained at the constant temperature of 70°C and time is immediately recorded using a stopwatch. At regular time intervals, a test tube is placed in an ice-cold water bath and the remaining acid is titrated with a sodium hydroxide solution ($Na^+ + HO^-$) in the presence of a suitable indicator.
The results obtained make it possible to plot the curve representing the change of the number of moles of the ester formed versus time ($n_{ester}$ formed = f (t) :




2.1 Explain why it is necessary to place the test tubes in the ice before titration.
2.2 Write, using the condensed structural formulas of organic species, the equation of the titration reaction of the carboxylic acid with the sodium hydroxide solution.

3 - **Analysis of the results**

3.1 Using the preceding curve calculate the yield of the reaction. Conclude.

3.2 Using the experimental value of the number of moles of ester formed $n_{ester}$ , determine the value of the equilibrium constant K. Is it coherent with the value provided in part 1?

3.3 Explain how to determine graphically the rate of the reaction at an instant t.

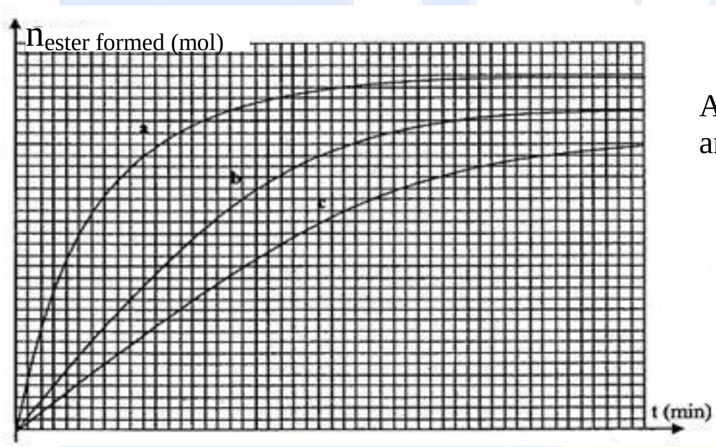
3.4 Compare the rates $r_1$ (at $t = t_1$) and $r_2$ (at $t = t_2 > t_1$) and justify the change of the value of the rate of the reaction with respect to time.

4 - **Influence of the Experimental Conditions**

Three other experiments are carried out in a similar way of the experiment n°1 but while varying the experimental conditions (temperature, initial number of moles of the reactants) according to the table below:

| Number of moles (mol) | Experiment nº1 | Experiment nº2 | Experiment nº3 |
|---|---|---|---|
| Carboxylic Acid | 0.10 | 0.10 | 0.20 |
| Menthol | 0.10 | 0.10 | 0.10 |
| Temperature (ºC) | 70 | 20 | 70 |

Curves of $n_{ester}$ formed = f (t) are plotted again. The obtained shapes are given below.




Allocate, by justifying your answer, the curves a, b and c to the experimental conditions 1.2 and 3.

**Entrance Exam 2010-2011** **Time: 1 hour**

**Solution of Chemistry** **July 04, 2010**

### First Exercise
### Ammonia

1.1- The equation of the reaction of ammonia with water is: $NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$. Its constant is

1.2- $Kc = \dfrac{[NH_4^+][HO^-]}{[NH_3]} = \dfrac{[NH_4^+][HO^-]}{[NH_3]} \times \dfrac{[H_3O^+]}{[H_3O^+]} = \dfrac{K_e}{K_a}$.

The constant $Kc = \dfrac{[HO^-]^2}{[NH_3]} = \dfrac{[HO^-]^2}{C} = \dfrac{10^{-14}}{10^{-9.2}} = 10^{-4.8} = 1.58\times10^{-5}$ ;

$[HO^-] = (1.58\times10^{-5} \times 1.00\times10^{-2})^{1/2} = 4.0\times10^{-4}$ mol.L$^{-1}$ and

$pH = 14 + \log [HO^-] = 14 + \log 4.0\times10^{-4} = 10.6$.

2.1- The equation of the reaction is: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

2.2- The relation $pH = pKa + \log \dfrac{[NH_3]}{[NH_4^+]}$ permits to calculate this ratio. $10 = 9.2 + \log \dfrac{[NH_3]}{[NH_4^+]}$

$\log \dfrac{[NH_3]}{[NH_4^+]} = 0.8$ and $\dfrac{[NH_3]}{[NH_4^+]} = 6.30$.

2.3- For a pH = 10 we have: $\dfrac{[NH_3]}{[NH_4^+]} = 6.30$ and $[NH_4^+] = \dfrac{2.00}{6.30} = 0.317$ mol.L$^{-1}$.

The mass of $NH_4Cl$ is $m = 1\times0.317\times53.5 = 17.0$ g.

2.4.1- The equation of the reaction of $H_3O^+$ ions with the buffer solution is:

$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$. The constant of this reaction is $K_R = 10^{\Delta pKa}$ with

$\Delta pKa = pKa(NH_4^+/NH_3) - pKa(H_3O^+/H_2O) = 9.2 - 0 = 9.2$. $K_R = 10^{9.2} >> 10^4$. This reaction is than total.

2.4.2- The number of moles of $NH_3$ which reacted with ions $H_3O^+$ is equal to the number of moles of $NH_4^+$ formed = n $H_3O^+ = 2.0\times10^{-3}$ mol. Therefore n $(NH_3) = 2.00\times80\times10^{-3} - 2.0\times10^{-3} = 0.160 - 0.002 = 0.158$ mol.

$[NH_3] = \dfrac{0.158}{0.1} = 1.58$ mol.L$^{-1}$. The number of moles of $NH_4^+$ in 80 mL is $0.317\times80\times10^{-3} = 25.36\times10^{-3}$ mol which becomes at equivalence: n $(NH_4^+) = 0.02736$ mol. Therefore: $[NH_4^+] = 0.2736$ mol.L$^{-1}$.

2.4.3- pH = 9.2 + log $\frac{1.58}{0.2736}$ = 9.96. This value is practically equal to 10. So, a buffer solution is used to control the pH of the reacting medium.

**Second Exercise**
**Kinetic of the reaction of synthesis of peppermint**

1.1- 1.1 - Menthol belongs to the chemical family of alcohols, because the hydroxyl group is related to a tetrahedral carbon atom. It is a secondary alcohol.

1.2- The name and the condensed structural formula of the carboxylic acid which, by reaction with menthol, makes it possible to synthesize menthyl ethanoate is ethanoic or acetic acid: $CH_3$-COOH.

1.3- The equation of synthesis reaction of the ester is:

$$CH_3\text{-}COOH + ROH \rightleftharpoons CH_3\text{-}COOR + H_2O$$

2.1- The test tubes are placed in the ice before titration in order to carry out a kinetic blocking the composition of the reacting medium does not change any more because the reaction of titration must be single.

2.2 The equation of the reaction associated to with the titration of the carboxylic acid solution is:

$$CH_3\text{-}COOH + HO^- \rightarrow CH_3\text{-}COO^- + H_2O$$

3.1- After a certain time, it is noted that the curve n(ester) = f (t) has a horizontal asymptote which intersects with the ordinates axis at $n_{end}$= 0.06 mol

The yield is y = $\frac{n_{end}}{n_{theoric}} = \frac{0.06}{0.1} = 0.6$ o ( 60 %).

It is concluded that the reaction of ester formation is not complete; it is reversible the hydrolysis reaction of the ester.

3.2- The constant associated to the equation of this reaction is:

$$K = \frac{[CH_3COOR][H_2O]}{[CH_3COOH][ROH]} = \frac{\frac{(n_{end})^2}{V^2}}{\frac{(0.10 - n_{end})^2}{V^2}} = \frac{0.06 \times 0.06}{(0.10 - 0.06)^2} = 2.25.$$

This value is in agreement with the value given (2.30) with a relative variation lower than: 0.05×100 / 2.3 =2.2 %.

3.3- To determine the rate of the reaction graphically the following approach is followed: at the date t considered, to trace the tangent with the curve n(ester) = f (t). The directing coefficient of this tangent gives $[dn/dt]_t$ which is equal to the rate of the reaction: $r_t = [dx/dt]_t$ expressed in mol.min$^{-1}$. Thus, we consider the coordinates of the two points rather distant from this tangent and we calculate the rate of the reaction.

3.4- Evolution of the value of the rate of the reaction in the course of time: at $t = t_1$ the slope of the tangent of the curve n(ester) = f (t) is higher than the slope of the tangent of the curve n(ester) = f (t) at $t = t_2$. Thus $v_1 > r_2$; it is concluded that the rate of the reaction decreases in the course of time: indeed the concentrations of the reactants, kinetic factor, decrease in the course of time.

4 - In the experiment n°3, two kinetic factors intervene: concentration of a reactant is doubled and the temperature of the medium is 70°C. The initial rate of the reaction will be greater and the equilibrium will be more quickly reached: thus the curve a.
In the experiment n°1, a kinetic factor intervenes: the temperature of the medium is 70°C. The initial rate of the reaction will be smaller (compared to the experiment n°3) and the equilibrium will be little less quickly be reached: thus curve b.
In the experiment n°2, the concentrations of the reactants and the temperature are weakest; in consequence the initial rate will be smallest and the equilibrium will be reached during a time rather long (curve c.