Entrance Exam 2012 – 2013 **CHEMISTRY** **Duration: 1H**
8 JULY 2012

First Exercise (13 points)
Buffer Solution

4 labeled bottles A, B, C and D containing each one of the following solutions: hydrochloric acid solution, sodium hydroxide solution, ethanoic acid solution, sodium ethanoate solution. These solutions have the same concentration C_0. The values of the pH of these solutions, at 25 ºC, are given in the following table:

Bottle	A	B	C	D
pH	2	3.3	12	9.1

Given:

Conjugate acid/base pair	H_3O^+/H_2O	CH_3COOH/CH_3COO^-	H_2O/HO^-
pKa at 25ºC	0.0	4.75	14.0

1- Identify the content of each bottle.
2- Determine C_0.
3- A volume of 75 mL of the ethanoic acid solution is mixed with 25 mL of the sodium hydroxide solution.
3.1- Write the equation of the reaction that takes place and determine its constant Kr.
3.2- Show that the pH of the obtained solution is: pH = 4.45.
4- Propose another way to prepare 100 mL of a buffer solution of the same pH = 4.45 starting with the solutions given above.
5- A volume V of the hydrochloric acid solution is mixed with an equal volume V of the ethanoic acid solution. The obtained mixture is called (M). Add progressively the sodium hydroxide solution to 20 mL of the mixture (M). The pH is measured at each addition. The results are given in the following table:

V_b (mL)	0	2	4	6	8	10	12	14
pH	2.6	3.1	3.4	3.8	4.1	4.2	4.4	4.7

V_b (mL)	16	18	20	22	24	26	28	30
pH	5.1	5.7	6.5	9.2	10.1	10.5	10.7	10.9

5.1- Plot the curve: pH= f(V_b). Take the following scale: 1 grid = 1 mL in abscissa axis and grids for 1 unit of pH in ordinate axis. 2

5.2- Based on the curve pH = f(V_b), determine the volume of the mixture (M) and that of the sodium hydroxide solution V_b needed to prepare 100 mL of a solution of pH = 4.45.

Second Exercise (7 points)
Esterification

A mixture of 0.200 mol of 2-propanol, 0.100 mol of propanoic acid and a few drops of sulfuric acid is heated until reaching the equilibrium state.

Given:

The percentage yield of an equimolar mixture of an carboxylic acid and an alcohol is: 67 % for a primary alcohol, 60 % for a secondary alcohol and 5 % for a tertiary alcohol.

1- Write, using for the organic compounds the condensed structural formulas, the equation of the reaction.

2- Give the name of the organic product obtained.

3- Specify for each following mixture if it can correspond to the equilibrium state.

Mixture	Acid (mol)	Alcohol (mol)	Ester (mol)	Water (mol)
1	0.050	0.150	0.050	0.050
2	0	0.100	0.100	0.100
3	0.022	0.122	0.078	0.078

4- Determine the equilibrium constant, Kc, knowing that the mixture 3 represents the equilibrium state.

Entrance Exam 2012 – 2013 **Solution of Chemistry** **Duration: 1H**
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First Exercise (13 points)
Buffer Solution

1- The 4 solutions have the same concentration of which two are acids, a strong one (hydrochloric acid; HCl) and a weak acid (ethanoic acid; CH_3COOH). The other two solutions are bases; a strong one (sodium hydroxide; NaOH) and a weak one (sodium ethanoate; CH_3COONa).

- The solution of least pH value (pH = 2) corresponds to the strong acid HCl (bottle A).
- The solution of greatest pH value (pH = 12) corresponds to the strong base NaOH (bottle C).
- The solution of pH = 3.3 < 7 corresponds to the weak acid CH_3COOH (bottle B).
- The solution of pH = 9.1 > 7 corresponds to the weak base CH_3COONa (bottle D).

(4 points)

2- $[H_3O^+] = 10^{-pH} = 1 \times 10^{-2} mol.L^{-1}$ **(1 point)**

3.1- The equation of the reaction is: $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$ **(0.5 point)**

Kr = $10^{pKa_2 - pKa_1} = 10^{14-4.75} = \mathbf{10^{9.25} = 1.78 \times 10^9}$ **(0.5 point)**

3.2- We can draw the following table:

State	Advance (mmol)	CH_3COOH +	HO^- →	CH_3COO^- +	H_2O
Initial	X = 0	0.75	0.25	0	excess
final	Xf = 0.25	0.50	0	0.25	ecxess

$pH = pKa + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$; $pH = 4.75 + \log\frac{(0.25)}{(0.50)}$; $pH = 4.75 + \log(0.5)$

⇨ **pH = 4.45** **(2 points)**

4- It is required of decreasing the pH of the solution of ethanoate by the addition of acid, either of hydrochloric acid or of ethanoic acid.

- **<u>Case of hydrochloric acid</u>**

$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$

State	Advance (mmol)	CH_3COO^- + H_3O^+ → CH_3COOH + H_2O			
Initial	X = 0	V1 x 10^{-2}	V1 x 10^{-2}	0	excess
final	Xf = 0.25	V1 x 10^{-2}-Xf	V2 x 10^{-2}- Xf	V1 x 10^{-2}-Xf	ecxess

With V1 + V2 = 100 mL, V2 x 10^{-2}- Xf = 0 and $\frac{V1 \times 10^{-2} - Xf}{Xf}$ = 0.5; we conclude:
1.5 Xf = V1 x 10^{-2} and Xf = V2 x 10^{-2}; 1.5 V2 = V1
So, **V2 = 40 mL and V1 = 60 mL.** **(2 points)**

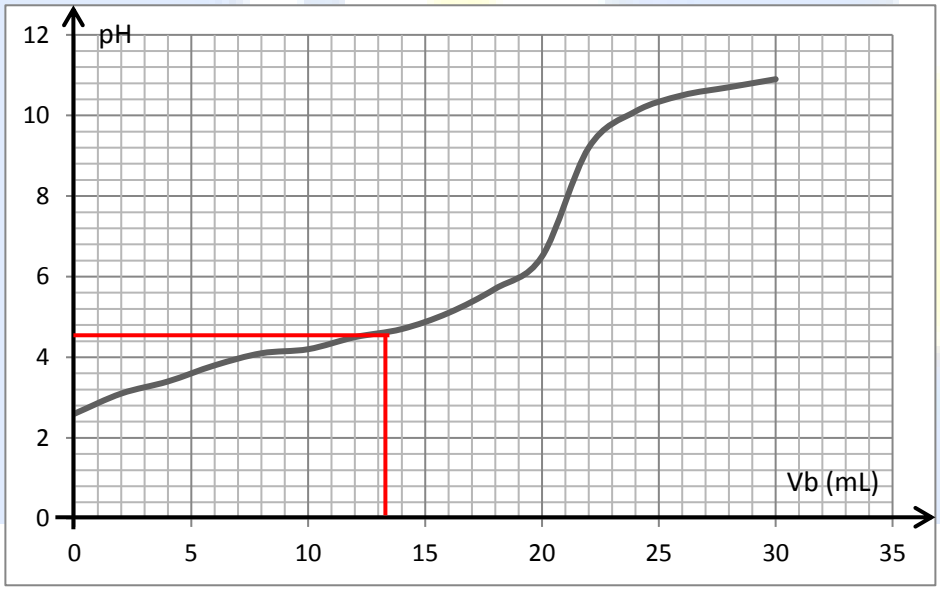
- **<u>Case of ethanoic acid</u>**

$$CH_3COOH + CH_3COO^- \rightarrow CH_3COOH + CH_3COO^-$$

With : V1 + V2 = 100 mL and V2 = 0.5 V1

We conclude: V1 = 66.67 mL and V2 = 33.33 mL. **(2 points)**

5.1- The curve is:



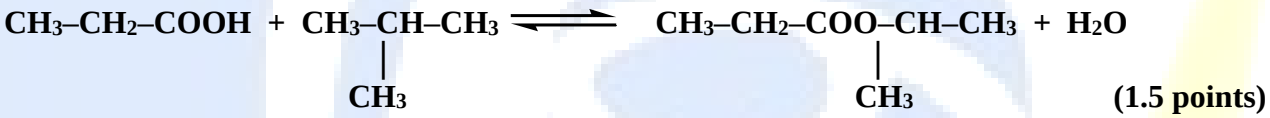
(2 points)

5.2- The curve shows that at pH = 4.45 correspond to the volume added of basic solution NaOH is 13.3 mL. The total volume in the beaker is then: 20 + 13.3 = 33.3 mL = $\frac{100}{3}$

To obtain100 mL, it is thus necessary to take Vm = 60 mL of the mixture (M) and Vb = 40 mL of the bacic solution to prepare 100 mL of pH = 4.45. **(1 points)**

Second Exercise (7 points)
Esterification

1- The equation of the reaction is:



(1.5 points)

2- The product obtained is: 2-propyl propanoate. **(0.5 points)**

3- The alcohol is secondary alcohol, for **equimolar** mixture the percentage yield is 60 %, since:

- The initial mixture is not equimolar, the percentage yield must exceed 60 %, compared to the limiting reactant, and the number of moles of ester must be higher than 0.060 mol, therefore the mixture 1 cannot correspond to the mixture at equilibrium (%y = 50 %)
- The esterification reaction is incomplete reaction, the acid does not disappear completely, and therefore mixture 2 cannot correspond to the mixture at equilibrium (%y = 100%).

- The percentage yield in mixture 3 is 78 %, for secondary alcohol and for non-equimolar initial mixture (exceeds 60%), so this percentage yield may be able to correspond to an equilibrium state. **(3 points)**

4- The equilibrium constant Kc is:

$$Kc = \frac{[ester][water]}{[alcohol][acid]} = \frac{\frac{(0.078)(0.078)}{V \ x \ V}}{\frac{(0.122)(0.022)}{V \ x \ V}} = 2.267$$ **(2 points)**