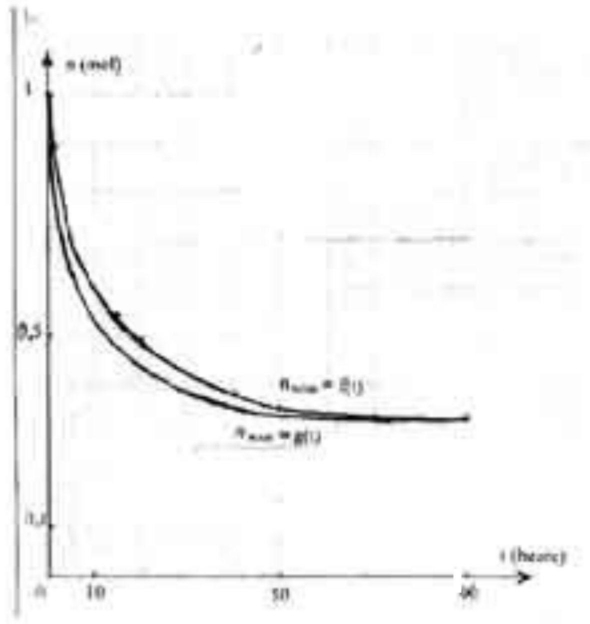
Marking Scheme **Chemistry** **2^{nd} session 2004**

First exercise (6.5 points)

Expected Answers	Comments
I-  2 - The increase in temperature speeds up the rate of the reaction. Since the reaction is athermic, the increase in temperature does not affect the composition of the reaction mixture at equilibrium. The shape of the curve $n_{acid} = g(t)$ is represented on th **t (hours)** I - 1- $RCOOH_{(\ell)} + R'OH_{(\ell)} \rightleftharpoons RCOOR'_{(\ell)} + H_2O_{(\ell)}$ Initial state 1 mol 1 mol 0 0 At time t (1- x) mol (1- x) mol x mol x mol 2- The equilibrium constant, K_c, is given by: $K_c = \frac{[RCOOR'][H_2O]}{[RCOOH][R'OH]}$. The concentrations, at equilibrium, are: $[RCOOR'] = [H_2O] = \frac{0.33}{V}$ $mol.L^{-1}$ and $[RCOOH] = [R'OH] = \frac{1-0.33}{V} = \frac{0.67}{V}$ $mol.L^{-1}$. So : $K_c = 4$. 3- Kc is a constant that depends only on temperature. So the presence of sulphuric acid does not affect the value of K_c . 4- At $t = \infty$, the equilibrium will be restablished, we have then: $n_{acid} = (2 - x)$ mol ; $n_{alcohol} = (1 - x)$ mol and $n_{ester} = n_{water} = x$ mol	

so:

$$4 = \frac{\frac{x^2}{V^2}}{\frac{(2-x)}{V}\frac{(1-x)}{V}}$$. The calculation gives: $x^2 = 4\,(2 + x^2 - 3x)$.

$3x^2 - 12x + 8 = 0$. The solution of this equation gives two values : $x' = 3.15 > 1$, rejectable value and $x'' = 0.845$ acceptable value, the amount of ester at infinity is then:

$n_{ester} = 0.845$ mol.

The addition of an excess of carboxylic acid shifts the equilibrium in the forward direction to form more ester.

In the presence of a big amount of the acid the yield of the reaction tends to its maximum value (n_{ester} tends to 1, and the reaction becomes approximately total).

Second exercise (7.5 points)

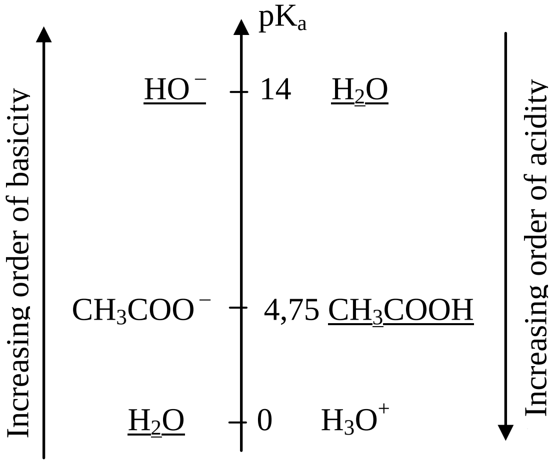
Expected Answers	Comments

I-

1- The orange colour means that the pH of the solution is between the two values: 3.1 and 4.4. This value is > $-\log C_1 = 2$, which shows that the dissociation of ethanoic acid is partial and consequently it is a weak acid.

2-

a)



b) The equation of the predominant reaction is the reaction that takes place between the stronger acid and the stronger base introduced in considerable amounts;

$$CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O.$$

c) $K_R = 10^{\Delta pKa}$.

$\Delta pKa = pKa\,(H_2O/HO^-) - pKa\,(CH_3COOH/CH_3COO^-) = 14 - 4.75$

$K_R = 10^{9.25} >> 10^4$. The reaction is total.

d) The relation pH = pKa + log $\frac{[CH_3COO^-]}{[CH_3COOH]}$ permits to calculate the ratio $\frac{[CH_3COO^-]}{[CH_3COOH]}$.

$\log\frac{[CH_3COO^-]}{[CH_3COOH]} = 8.4 - 4.75 = 3.65$, where: $\frac{[CH_3COO^-]}{[CH_3COOH]} \approx 4467$. The concentration of the acid is practically null. The acid had almost, reacted completely.

II –

1- The equipment: 10 mL volumetric pipet, beaker and pipet filler in order to take V_a . 25 mL graduated burette, 100 mL beaker, magnetic stirrer and magnetic bar in order to perform the titration.

2- At equivalence, we have:
n CH_3COOH in V_a = n HO^- in 10.1 mL of basic solution. Where in a solution: n solute (mol) = C ($mol.L^{-1}$)x V solution (L):
The concentration of ethanoic acid in solution (S) is:

$$C_{(S)} = \frac{0.1 \times 10.1 \times 10^{-3}}{10 \times 10^{-3}} = 0.101\,mol.L^{-1}.$$

3- The concentration of vinegar is = 1.01mol.L^{-1} because solution (S) is obtained by diluting the vinegar 10 times.
The mass of 100 mL of vinegar = 100 × 1.02 = 102g .
This mass contains $n = 1.01 \times 100 \times 10^{-3}$ = 0.101mol,so $m = 0.101 \times 60$ = 6.06g
The degree of acidity is then $6.06 \times \frac{100}{102} = 5.94°$.

Third exercise (6 points)

Expected Answers	Comments

I-

1-

(4) $CH_3 - C(=O) - O - CH_2 - CH_2 - CH_3$ and (5) $CH_3 - CH_2 - C(=O) - NH_2$

1- Propyl ethanoate — Propanamide

2- Functional isomers, because the first is an alcohol and the second is an ether.

3- This isomer should be an alkyl ethanoate. The last one has 3 atoms of carbon. The formula is then :

$CH_3 - C(=O) - O - CH(CH_3) - CH_3$

II-

1- The contents of flasks (a) and (b) are reducing agents. Only compound (1) (aldehyde) and compound (2) (secondary alcohol) are reducing agents. Since flask (a) gives a positive test with DNPH , therefore it contains in its molecule a carbonyl group. So it is propanal.
The content of flask (b) is then a secondary alcohol : 2 – butanol.

2- $CH_3 - CH_2 - CHOH - CH_3 + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow$

$CH_3 - C(=O) - O - CH(CH_3) - CH_2 - CH_3 + CH_3 - C(=O) - OH$

III- 1-In order to prepare (3), starting from ethanol, the equation of the reaction is: 2 $CH_3 – CH_2 – OH \rightarrow CH_3 – CH_2 – O – CH_2 – CH_3 + H_2O$. 2- $CH_3 – CH_2 – CHO + ½ O_2 \rightarrow CH_3 – CH_2 – COOH$ $CH_3 – CH_2 – COOH + NH_3 \rightarrow CH_3 – CH_2 – CO – NH_2 + H_2O$	