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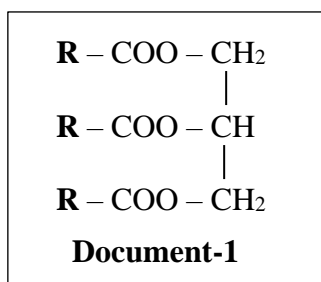
مسابقة في مادة الكيمياء  
المدة: ساعتان

**This Exam Includes Three Exercises. It Is Inscribed On 4 Pages Numbered from 1 to 4.  
The Use Of A Non-Programmable Calculator Is Allowed.**

**Answer The Three Following Exercises:**

### **Exercise 1 (7 points) From Butter to a Perfumed Compound**

Butyric or glyceryl tributyrate is a triglyceride found in butter.  
The general formula of triglyceride is represented in **document-1**.



The aim of this exercise is to study the preparation of an organic compound used in perfumery from butter.

**Given:** - Molar Masses in  $\text{g}\cdot\text{mol}^{-1}$ :  $M(\text{C}) = 12$ ;  $M(\text{H}) = 1$ ;  $M(\text{O}) = 16$   
- **R** is an alkyl group of formula  $\text{C}_n\text{H}_{2n+1}$

#### **1. Structure of Butyric**

Referring to **document-1**:

- 1.1.** Show that the formula of **R** is  $\text{C}_3\text{H}_7$ , knowing that the molar mass of butyric is  $M = 302 \text{ g}\cdot\text{mol}^{-1}$ .
- 1.2.** Write the condensed structural formula of butyric.

#### **2. Synthesis of an Ester (E)**

Butyric can be used to manufacture an ester (E), used in perfumery, according to the reactions given in **document-2**.

**Reaction 1:**  $\text{Butyric} + 3 (\text{Na}^+ + \text{HO}^-) \rightarrow 3 (\text{C}_3\text{H}_7 - \text{COO}^- + \text{Na}^+) + (\text{G})$  (**Saponification reaction**)

**Reaction 2:**  $\text{C}_3\text{H}_7 - \text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{C}_3\text{H}_7 - \text{COOH} + \text{H}_2\text{O}$

**Reaction 3:**  $\text{C}_3\text{H}_7 - \text{COOH} + 2\text{-propanol} \rightleftharpoons (\text{E}) + \text{H}_2\text{O}$  (**Esterification reaction**)

**Document-2**

- 2.1.** Referring to **document-2**, specify whether each of the the following propositions is true or false.
  - 2.1.1.** The systematic name of the compound (G) is glycerol.
  - 2.1.2.** The ion  $\text{C}_3\text{H}_7 - \text{COO}^-$  is amphiphilic.
  - 2.1.3.** The sodium butanoate solution ( $\text{C}_3\text{H}_7 - \text{COO}^- + \text{Na}^+$ ) is neutral.
  - 2.1.4.** The **reaction 2** is an acid-base reaction.
- 2.2.** Write, using condensed structural formulas, the equation of the **reaction 3**. Give the systematic name of the ester (E).
- 2.3.** Specify whether the molecule of compound (E) is chiral.

### 3. Study of the Reaction 3

Starting from an equimolar mixture of  $C_3H_7 - COOH$  and 2-propanol, the yield of the esterification reaction (**reaction 3**) is 60 %.

**3.1.** Propose a way to increase the yield of this reaction starting from the same reactants.

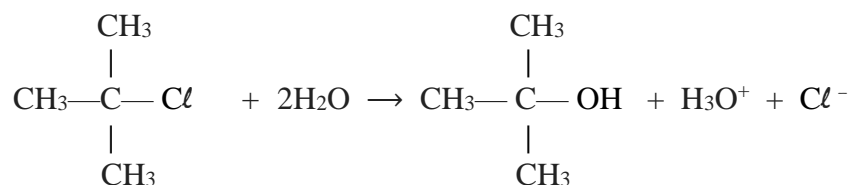
**3.2.** This reaction becomes complete when one of the reactants is replaced by its chlorinated derivative.

Write, using condensed structural formulas, the equation of this reaction.

### Exercise 2 (6 points)

### Kinetics of the Hydrolysis of t-Butyl Chloride

2-chloro-2-methylpropane, commonly known as t-butyl chloride, is a colorless organic compound belonging to the series of halogenoalkanes. When tert-butyl chloride is dissolved in water-acetone mixture, it reacts with water to form tert-butyl alcohol and hydrochloric acid in a slow and complete reaction that took place according to the equation shown below.



The aim of this exercise is to study the kinetic of this reaction.

**Given:** - Molar mass of tert-butyl chloride:  $M = 92.5 \text{ g}\cdot\text{mol}^{-1}$

- Density of tert-butyl chloride:  $d = 0.85 \text{ g}\cdot\text{mL}^{-1}$

#### 1. Preliminary Study

**1.1.** Give the systematic name of tert-butyl alcohol.

**1.2.** Specify its class.

**1.3.** What is observed when an excess of an orange acidified potassium dichromate solution is poured into a test tube containing tert-butyl alcohol? Justify.

#### 2. Kinetic Study

At the instant of time  $t = 0$ , a volume  $V = 1.0 \text{ mL}$  of t-butyl chloride is introduced into a flask containing water-acetone mixture, maintained at constant temperature  $T$ . The final volume of the reacting mixture is  $V_1 = 100.0 \text{ mL}$ . (Water is in large excess)

Using an appropriate method, the concentrations of hydronium ions are determined at different instants and the concentrations of tert-butyl chloride (noted  $[RCl]$ ) are deduced at these instants. The results are grouped in the table of **document-1**.

<b>t (min)</b>	0	15	30	45	60	75	90
<b><math>[RCl]</math> (<math>10^{-2}\text{mol}\cdot\text{L}^{-1}</math>)</b>	9.2	6.6	5.2	4.1	3.2	2.5	2.1

**Document-1**

**2.1.** Verify that the initial concentration of tert-butyl chloride  $[RCl]_0 = 9.2 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ .

**2.2.** Establish the relation between the concentration of hydronium ions,  $[H_3O^+]_t$ , formed at the instant of time  $t$  and the concentration of tert-butyl chloride,  $[RCl]_t$ , at the same instant  $t$ .

**2.3.** Plot the curve representing the change of the concentration of tert-butyl chloride as a function of time:  $[RCl] = f(t)$ , in the interval of time:  $[0 - 90 \text{ min}]$ .

Take the following scales:

In abscissa: 1 cm for 15 min ;

In ordinate: 1 cm for  $1.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ .

- 2.4. For each of the two following propositions, justify the correct one and correct the false one
- 2.4.1. The half-life time of this reaction is  $t_{1/2} = 38$  min.
- 2.4.2. As the concentration of the tert-butyl alcohol increases with time, the rate of its formation increases.
- 2.5. The same experiment is repeated but with only one modification: the reacting mixture is maintained at a temperature  $T'$  greater than  $T$ . Trace on the same graph of the part 2.3, the shape of the curve  $[RC\ell] = g(t)$  in the interval of time:  $[0 - 90 \text{ min}]$ .

### Exercise 3 (7 points)

### Acid-Base Reactions

The labels of three available flasks show the indications given in **document -1**.

Flask (1)	Flask (2)	Flask (3)
Benzoic acid crystals $M(C_6H_5COOH) = 122 \text{ g.mol}^{-1}$	Ethylamine aqueous solution percentage by mass = 33% Density = $0.914 \text{ g.mL}^{-1}$ $M(C_2H_5NH_2) = 45 \text{ g.mol}^{-1}$	Hydrochloric acid solution ( $H_3O^+ + Cl^-$ ) $C_a = 5 \times 10^{-2} \text{ mol.L}^{-1}$

**Document -1**

**Given:** - The study is carried out at  $25^\circ\text{C}$ .

- Ethylamine is a weak base.

-  $pK_a$  of Acid/Base pairs:

$pK_a(C_6H_5COOH/C_6H_5COO^-) = 4.2$  ;  $pK_a(C_2H_5NH_3^+/C_2H_5NH_2) = 10.8$ ;  $pK_a(H_2O/HO^-) = 14$

The aim of this exercise is to prepare acidic and basic solutions of same concentration  $C$  and to study some acid – base reactions.

#### 1. Preparation of Benzoic Acid Solution ( $S_1$ )

A mass  $m$  of benzoic acid crystals is introduced into a volumetric flask of 250 mL. Enough distilled water is added to dissolve the solid then distilled water is added to reach the line mark. A solution ( $S_1$ ) of benzoic acid of concentration  $C = 2 \times 10^{-2} \text{ mol.L}^{-1}$  is obtained.

1.1. Calculate the mass  $m$ .

1.2. Write the equation of the reaction of benzoic acid with water.

#### 2. Preparation of an Aqueous Ethylamine Solution ( $S_2$ )

It is required to prepare 1.0 L of an ethylamine solution ( $S_2$ ) of concentration  $C = 2 \times 10^{-2} \text{ mol.L}^{-1}$  starting from the solution of the flask (2).

2.1. Show that the volume that should be withdrawn from the flask (2) to realize this preparation is  $V = 3 \text{ mL}$ .

2.2. Choose, from the sets of **document-2**, the most convenient one to realize the above preparation.

Set 1	Set 2	Set 3
Volumetric pipet 5 mL	Graduated pipet 5 mL	Graduated cylinder 5mL
Volumetric flask 1000mL	Volumetric flask 1000mL	Erlenmeyer flask 1000 mL
Beaker 50 mL	Beaker 50 mL	Beaker 50 mL

**Document-2**

2.3. Specify, from the following propositions, the one that corresponds to the pH of the solution ( $S_2$ ).

a.  $\text{pH} = 12.3$

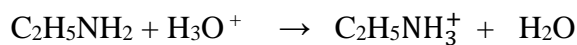
b.  $1.7 < \text{pH} < 7$

c.  $7 < \text{pH} < 12.3$

### 3. pH-metric Study

A hydrochloric acid solution of concentration  $C_a = 5 \times 10^{-2} \text{ mol.L}^{-1}$  is added progressively into a beaker containing a volume  $V_b = 20.0 \text{ mL}$  of the ethylamine solution ( $S_2$ ) of concentration  $C$ .

The equation of the complete reaction that took place is:



**3.1.** Justify the following statements:

**3.1.1.** The volume of the acid solution added to reach the equivalence point is 8 mL.

**3.1.2.** The pH at equivalence, based on the chemical species present at equivalence, is  $\text{pH}_E < 7$

**3.1.3.** The coordinates of the half equivalence point are ( $V_a = 4 \text{ mL}$ ;  $\text{pH} = 10.8$ ).

### 4. Acid-Base Mixture

A volume a volume  $V_1 = 72 \text{ mL}$  of the benzoic acid solution ( $S_1$ ) is mixed with a volume  $V_2 = 28 \text{ mL}$  of the above ethylamine solution ( $S_2$ ).

**4.1.** Write the equation of the complete reaction that took place in this mixture.

**4.2.** Determine the ratio  $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$  in the obtained solution, knowing that ethylamine is the limiting reactant.

**4.3.** Given the three following values of pH :

**a.**  $\text{pH} < 3.2$  ;

**b.**  $\text{pH} = 4$  ;

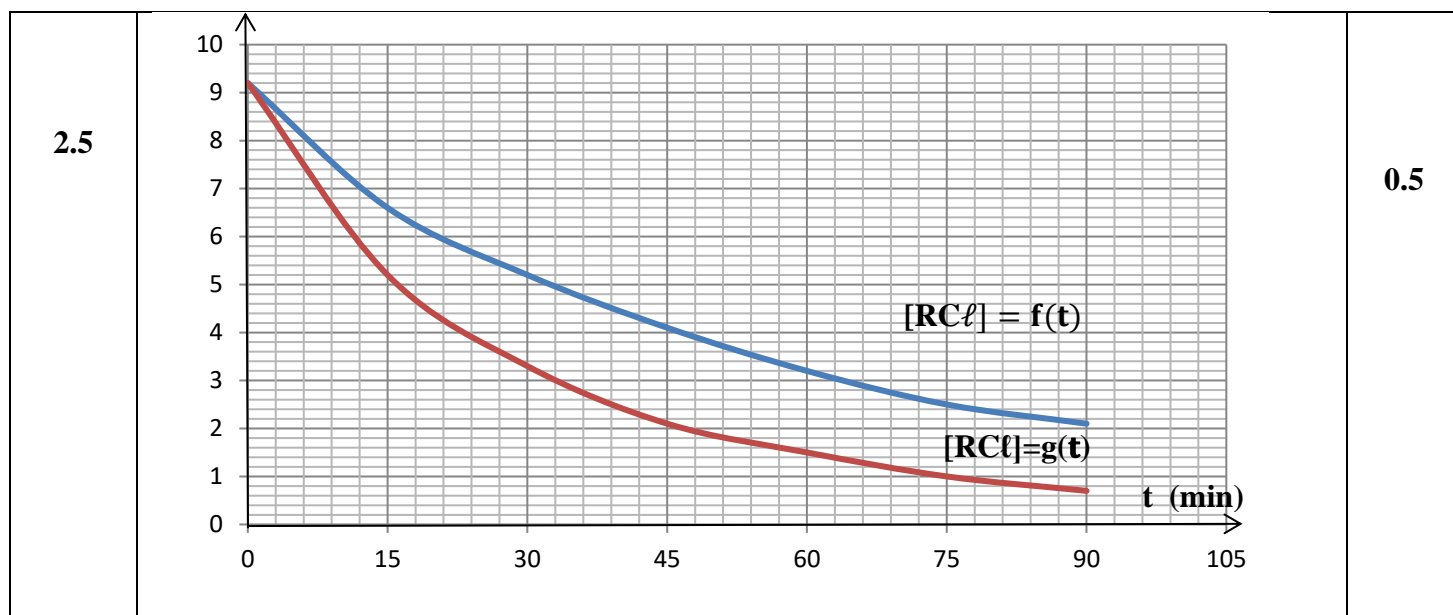
**c.**  $\text{pH} > 5.2$

Choose the one that corresponds to the pH of the obtained solution. Justify without calculation.

مشروع معيار التصحيح  
المادة: كيمياء

Exercise 1 (7 points)		From Butter to a Perfumed Compound	
Part of the Q	Answer		Mark
1.1	The molar mass of butyric acid is: $M = 3R + 6(12) + 6(16) + 5 = 302 \text{ g.mol}^{-1}$ , $M(R) = (302 - 173) \div 3 = 43 \text{ g.mol}^{-1}$ , R is an alkyl group of formula $C_nH_{2n+1} = 43$ , $12n + 2n+1 = 43$ , $n = 3$ , then formula of alkyl group R is $C_3H_7$		0.75
1.2	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH}_2 \\   \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH} \\   \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH}_2 \end{array}$		0.5
2.1.1	False. The systematic name of the compound (G) is 1,2,3 – propanetriol		0.75
2.1.2	True. The ion $C_3H_7 - \text{COO}^-$ has two ends: ( $C_3H_7 -$ ) is the tail which is lipophilic (or hydrophobic), and $\text{COO}^-$ is the head which is hydrophilic (or lipophobic), thus $C_3H_7 - \text{COO}^-$ is amphiphilic.		0.75
2.1.3	False. The sodium butanoate solution ( $C_3H_7 - \text{COO}^- + \text{Na}^+$ ) is basic, due to the presence of the ion $C_3H_7 - \text{COO}^-$ which is a basic species and $\text{Na}^+$ is a spectator ion.		0.75
2.1.4	True. Reaction 2 is an acid base reaction since there is a proton ( $\text{H}^+$ ) transfer from $\text{H}_3\text{O}^+$ to $C_3H_7 - \text{COO}^-$		0.75
2.2	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH} + \text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3 \rightleftharpoons \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 + \text{H}_2\text{O}$ <p>The systematic name of (E) 1-methylethylbutanoate.</p>		1
2.3	The molecule of compound (E) is not chiral since it doesn't contain an asymmetric carbon atom.		0.5
3.1	One can increase the yield of this reaction starting from the same reactants by using a non equimolar reacting mixture		0.5
3.2	The equation of the reaction using a chlorinated derivative is: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COCl} + \text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 + \text{HCl}$		0.75
Exercise 2 (6 points)		Kinetics of the Hydrolysis of t-Butyl Chloride	
Part of	Answer		Mark

the Q		
1.1	The systematic name of this alcohol is 2-methyl-2-propanol	0.5
1.2	This alcohol is a tertiary alcohol since the carbon bearing the hydroxyl group is linked to three alkyl groups.	0.5
1.3	Since the alcohol is a tertiary alcohol, then it doesn't undergo mild oxidation reaction with strong oxidizing agent such as potassium dichromate. The orange color of the potassium dichromate solution persists.	0.5
2.1	The initial concentration of tert-butyl chloride $[RCl]_0 = \frac{n(RCl)}{V_t} = \frac{m(RCl)}{M(RCl) \times V_t} = \frac{d \times v}{M(RCl) \times V_t} = \frac{0.85 \times 1}{92.5 \times 0.1} = 9.2 \times 10^{-2} \text{ mol.L}^{-1}$ .	0.5
2.2	$n_o(RCl) = n(RCl)_t + n(RCl)_{\text{disap}}$ $n(RCl)_{\text{disap}} = n(H_3O^+)_{\text{formed}}$ $n_o(RCl) = n(RCl)_t + n(H_3O^+)_{\text{formed}}$ $n(RCl)_t = n_o(RCl) - n(H_3O^+)_{\text{formed}}$ divided by $V_t$ $[RCl]_t = [RCl]_0 - [H_3O^+]_t$ , $[RCl]_t = 9.2 \times 10^{-2} - [H_3O^+]_t$	0.75
2.3	<p>The curve is :</p>	1
2.4.1	<p>True. The half-life time of a reaction is the time needed for the disappearance of half the initial quantity of RCl.</p> $[RCl]_{t_{1/2}} = (9.2 \times 10^{-2}) \div 2 = 4.6 \times 10^{-2} \text{ mol.L}^{-1}$ Graphically $t_{1/2} = 38 \text{ min}$	1
2.4.2	False. As the concentration of the tert-butyl alcohol increases with time, the concentration of the reactants decreases and since the concentration of reactants is a kinetic factor, so the rate of the formation of the alcohol decreases with time.	0.75
	$[RCl] (10^{-2} \text{ mol.L}^{-1})$	



<b>Exercise 3 (7 points)</b>		<b>Acid-Base Reactions</b>
<b>Part of the Q</b>	<b>Answer</b>	<b>Mark</b>
<b>1.1</b>	$m = C \times V \times M = 0.02 \times 0.25 \times 122 = 0.005 \times 122 = 0.61 \text{ g}$	<b>0.5</b>
<b>1.2</b>	Benzoic acid is a weak acid $\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+$	<b>0.5</b>
<b>2.1</b>	During dilution, the number of moles of solute is conserved: $n = C \times V = 0.02 \times 1 = 0.02 \text{ mol}$ mass of $\text{C}_2\text{H}_5\text{NH}_2$ present in 1 L of solution ( $S_2$ ) = $0.02 \times 45 = 0.9 \text{ g}$ mass of solution of the flask (2) : $m = \frac{0.9 \times 100}{33} = 2.72 \text{ g}$ volume of solution of the flask (2): $V = \frac{2.72}{0.914} = 3 \text{ mL}$	<b>1</b>
<b>2.2</b>	The most convenient set is the set (2)	<b>0.5</b>
<b>2.3</b>	Since $\text{C}_2\text{H}_5\text{NH}_2$ is a weak base so its pH is greater than 7 but less than 14 + log C , $14 + \log C = 12.3$ The answer is c	<b>0.5</b>
<b>3.1.1</b>	At the equivalence point: $n(\text{H}_3\text{O}^+)_{\text{added to reach equivalence}} = n(\text{C}_2\text{H}_5\text{NH}_2)_{\text{introduced into the beaker}}$ $C_3 \times V_E = C \times V_b \Rightarrow V_E = \frac{C \times V_b}{C_3} = \frac{0.02 \times 20}{0.05} = 8 \text{ mL.}$	<b>0.75</b>
<b>3.1.2</b>	The chemical species present in solution at equivalence (other than $\text{H}_2\text{O}$ ) are: $\text{C}\ell^-$ which is a spectator ion. $\text{C}_2\text{H}_5\text{NH}_3^+$ : the conjugate weak acid of the weak base $\text{C}_2\text{H}_5\text{NH}_2$ . therefore the solution at equivalence is acidic and its pH is less than 7	<b>0.5</b>

<p><b>3.1.3</b></p>	<p>The equivalence point: <math>V_E = 8\text{mL}</math>          At half equivalence <math>V = \frac{V_E}{2} = 4\text{ mL}</math> , <math>\text{pH} = \text{pK}_a = 10.8</math>          then the coordinates of the half equivalence point are:          (<math>V_a = 4\text{ mL}</math>, <math>\text{pH} = 10.8</math>).</p>	<p><b>0.5</b></p>																								
<p><b>4.1</b></p>	<p>The equation of the reaction:  <math>\text{C}_6\text{H}_5\text{COOH} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{C}_6\text{H}_5\text{COO}^-</math></p>	<p><b>0.5</b></p>																								
<p><b>4.2</b></p>	<p>since ethylamine is the limiting reactant then:</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td></td> <td><math>\text{C}_6\text{H}_5\text{COOH}</math></td> <td>+</td> <td><math>\text{C}_2\text{H}_5\text{NH}_2</math></td> <td><math>\rightarrow</math></td> <td><math>\text{C}_2\text{H}_5\text{NH}_3^+</math></td> <td>+</td> <td><math>\text{C}_6\text{H}_5\text{COO}^-</math></td> </tr> <tr> <td>Initial state</td> <td><math>C \times V_1</math></td> <td></td> <td><math>C \times V_2</math></td> <td></td> <td>0</td> <td></td> <td>0</td> </tr> <tr> <td>Final state</td> <td><math>C \times V_1 - C \times V_2</math></td> <td></td> <td>0</td> <td></td> <td><math>C \times V_2</math></td> <td></td> <td><math>C \times V_2</math></td> </tr> </table> $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{n_{\text{C}_6\text{H}_5\text{COO}^-} \div V_t}{n_{\text{C}_6\text{H}_5\text{COOH}} \div V_t} = \frac{(C \times V_2)}{(C \times V_1) - (C \times V_2)}$ $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{V_2}{V_1 - V_2} = \frac{28}{72 - 28} = 0.636$		$\text{C}_6\text{H}_5\text{COOH}$	+	$\text{C}_2\text{H}_5\text{NH}_2$	$\rightarrow$	$\text{C}_2\text{H}_5\text{NH}_3^+$	+	$\text{C}_6\text{H}_5\text{COO}^-$	Initial state	$C \times V_1$		$C \times V_2$		0		0	Final state	$C \times V_1 - C \times V_2$		0		$C \times V_2$		$C \times V_2$	<p><b>1</b></p>
	$\text{C}_6\text{H}_5\text{COOH}$	+	$\text{C}_2\text{H}_5\text{NH}_2$	$\rightarrow$	$\text{C}_2\text{H}_5\text{NH}_3^+$	+	$\text{C}_6\text{H}_5\text{COO}^-$																			
Initial state	$C \times V_1$		$C \times V_2$		0		0																			
Final state	$C \times V_1 - C \times V_2$		0		$C \times V_2$		$C \times V_2$																			
<p><b>4.3</b></p>	<p><math>\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = 0.636</math>          Since <math>[\text{C}_6\text{H}_5\text{COO}^-] &lt; 10 [\text{C}_6\text{H}_5\text{COOH}]</math>, <math>\text{C}_6\text{H}_5\text{COO}^-</math> doesn't predominates <math>\text{C}_6\text{H}_5\text{COOH}</math> in the solution. So <math>\text{pH} &lt; \text{pK}_a + 1 = 5.2</math></p> <p>Similarly, <math>\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{1}{0.636} = 1.572</math>, <math>[\text{C}_6\text{H}_5\text{COOH}] &lt; 10 [\text{C}_6\text{H}_5\text{COO}^-]</math>,  <math>\text{C}_6\text{H}_5\text{COOH}</math> doesn't predominate <math>\text{C}_6\text{H}_5\text{COO}^-</math> in the solution. So <math>\text{pH} &gt; \text{pK}_a - 1 = 3.2</math>          The answer is <b>b</b>.</p>	<p><b>0.75</b></p>																								