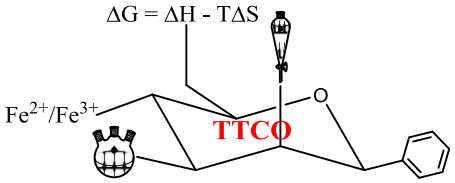


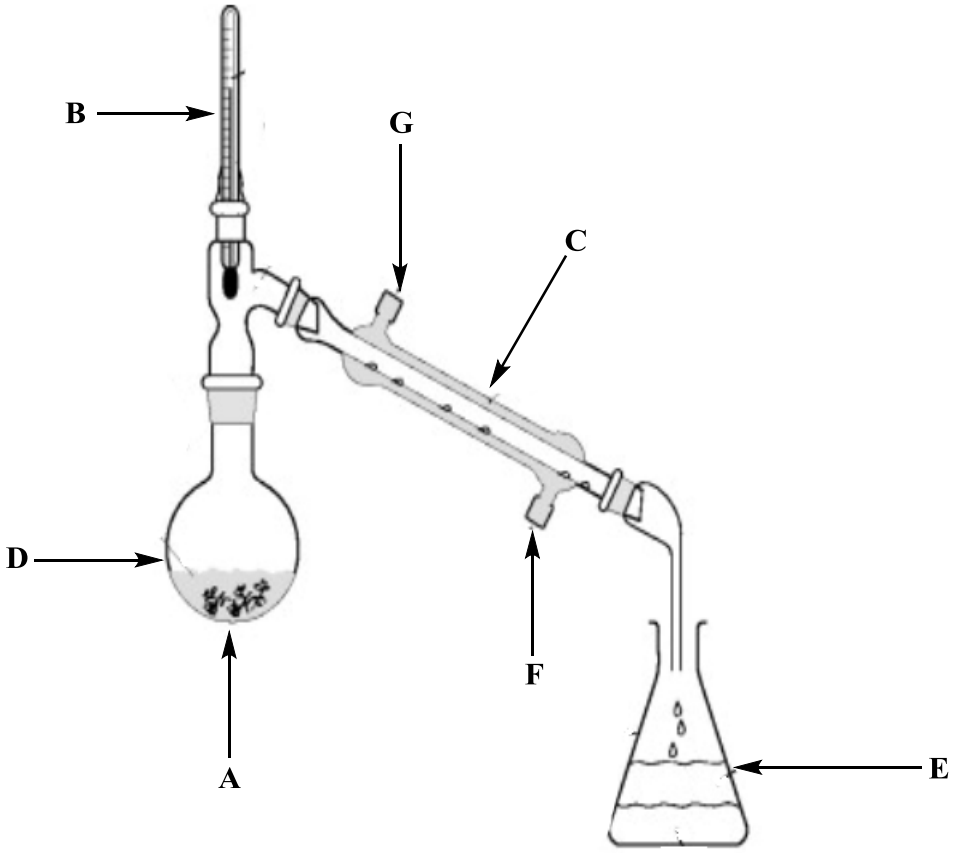
Trinidad and Tobago Chemistry Olympiad

Round 2 - Level A

INSTRUCTIONS TO CANDIDATES:

1. **Do not turn this page until you are told to do so**.
2. This paper consists of **ten (10)** numbered pages.
3. There are **five (5)** questions: Answer **all** questions.
4. The examination duration is **3 hours**.
5. The total number of marks = **93 marks**.
6. In addition to this question paper, you should also have an answer booklet and graph paper.
7. Show **ALL** working. The majority of marks are awarded for appropriate statements, descriptions, and explanations.
8. The use of non-programmable calculators is allowed.
9. A Periodic Table will not be provided.

1. *The first recorded chemist was a woman by the name of Tapputi, who lived in ancient Mesopotamia. She, along with her assistant (-)-ninu, were responsible for making perfumes in the kingdom. Many of their techniques, and perfume components, have persisted to modern times. One of these procedures is the distillation of fragrances from plants. Consider a modern distillation set-up:*



*(a) Identify the process represented by **A**.* ***(2 marks)***

- Heating (2 marks)

*(b) Identify the apparatus represented by **B** to **E**.* ***(8 marks)***

- B: Thermometer (2 marks)
- C: Condenser (2 marks)
- D: Round bottom flask / Distillation flask (2 marks)
- E: Conical flask / Erlenmeyer flask / Collecting flask (2 marks)

*(c) The processes **F** and **G** represent "water out" or "water in".*

*(i) Identify which is **F**, and which is **G**.* ***(2 marks)***

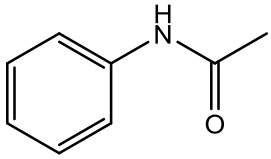
- F: water in (1 mark)
- G: water out (1 mark)

(ii) Justify your choice i.e. why is it not opposite to that which you have identified in (i)?

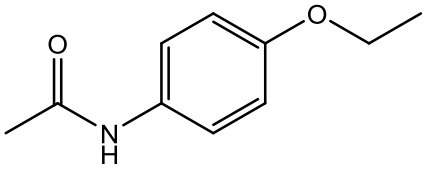
(2 marks)

- There are two justifications for why this is the preferred arrangement. Only one is required for full marks: (2 marks)
- Ensures that the condenser is completely filled with water at any time. If it was set up in the opposite manner, and the rate of water flow in was slower (low water pressure) than the rate of outflow (by gravity), at some point there may be regions where the vapour is not being cooled sufficiently to be able to condense.
- Optimal cooling and minimization of thermal shock/stress occurs when there is countercurrent flow i.e. - hot vapour flowing in one direction, and the cooling medium (water) flowing in the opposite.

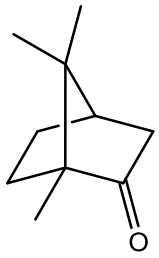
(d) You are provided with a solution of the following drugs (with their melting points identified):



Acetanilide
m.p. = 134 ^{o}C



Phenacetin
m.p. = 114 ^{o}C



Camphor
m.p. = 176 ^{o}C

(i) Which compound: water (b.p. = 100 °C) or ethanol (b.p. = 78 °C), is most likely the solvent used to prepare the above solution? Justify your answer. ***(3 marks)***

- These are all organic compounds, with intermolecular forces of attraction being hydrogen bonding and Van der Waals forces; and are likely to dissolve in a solvent whose prevalent molecular forces of attraction are similar ("like dissolves like"). (1 mark)
- Water will primarily (**not only**) dissolve ionic / ionizable compounds. (1 mark)
- Ethanol has both hydrogen bonding and Van der Waals forces, and readily dissolves many (**not all**) organic compounds. (1 mark)

Ethanol therefore is the most likely solvent used to prepare the solution.

(ii) Is simple distillation of the solution an appropriate method to separate the three drugs and obtain purified amounts of each? Justify your answer. ***(3 marks)***

- Simple distillation is used to separate two (or more) components of a mixture that have significantly different boiling points, and it is most efficient when these species do not form azeotropes. (1 mark)
- In the above mixture, the lowest boiling component (the first to be distilled off) is the solvent (ethanol), which will then leave behind the three solids. Continued heating will not effectively separate these three solids from each other. (1 mark)

- Simple distillation is therefore not an appropriate method for separation of this mixture.
(1 mark)

For consideration: *How would a solid mixture of the above three compounds be separated? - Column Chromatography would be the most straightforward technique. Recrystallization may also work, provided that suitable solvents can be found.*

2. Chalcopyrite is a naturally occurring mineral with the formula: $CuFeS_2$.

(a) Calculate the oxidation number of the iron in this compound. ***(3 marks)***

- The principal metallic ores involving sulphur are the sulphides, in which the oxidation number of sulphur = - 2.
- The common oxidation number of copper is = + 2.

The sum of all oxidation states of atoms present in a neutral compound = 0
Assigning oxidation numbers:

1 Cu (+ 2) + Fe + 2 x S (- 2) = 0 (2 marks)
+ 2 + Fe - 4 = 0
Fe = + 2 (1 mark)

(b) What is the % mass composition of copper in 1 g of Chalcopyrite?
Ar: Cu = 64; Fe = 56; S = 32 ***(4 marks)***

- 1 mole of Chalcopyrite = 64 + 56 + (2 x 32) (1 mark)
= 184 g (1 mark)

- 184 g Chalcopyrite = 64 g Cu (1 mark)
- % mass composition = 64 / 184 x 100
= 34.8 % (1 mark)

(c) Copper metal can be extracted by the complete combustion of Chalcopyrite in the presence of oxygen and silica (SiO_2). The other products of this reaction are: sulphur dioxide and ferrosilite ($FeSiO_3$). You have 1 kg of Chalcopyrite which you subject to this reaction.

(i) Write the balanced equation for this reaction. ***(3 marks)***

$$2CuFeS_2 + 5O_2 + 2SiO_2 \longrightarrow 2Cu + 4SO_2 + 2FeSiO_3$$

or

$$CuFeS_2 + 5/2O_2 + SiO_2 \longrightarrow Cu + 2SO_2 + FeSiO_3$$

- Representing correct formulae of reactants and products (1 mark)
- Correctly balanced equation (2 marks)

(ii) What mass of copper metal will be produced? ***(3 marks)***

- From the balanced equation:
- 1 mole Chalcopyrite = 1 mole Cu (1 mark)
- 184 g Chalcopyrite = 64 g Cu
- 1000 g Chalcopyrite = 64/184 x 1000 g Cu (1 mark)
  = 347.8 g Cu metal produced (1 mark)

(iii) Assuming that the reaction occurs at 298 K, what is the volume of sulphur dioxide expected to be produced at this temperature? State any further assumptions.

(6 marks)

- From the balanced equation:
- 1 mole Chalcopyrite = 2 moles SO_2 (1 mark)
- 184 g Chalcopyrite = 2 moles SO_2
- 1000 g Chalcopyrite = 2/184 x 1000 moles SO_2
  = 10.9 moles SO_2 (1 mark)

Assuming RTP i.e. pressure = 1 atm (1 mark) and

SO_2 behaves like an ideal gas (1 mark)

1 mole of gas = 24.0 dm^3 (1 mark)

10.9 moles = 10.9 x 24.0 dm^3

= 260.9 dm^3 of SO_2 produced (1 mark)

(d) Chalcopyrite undergoes various reactions. One of these is shown below, with the respective reactants and products:

$$CuFeS_2\ (s) + Fe_2(SO_4)_3\ (s) + H_2O\ (l) \longrightarrow CuSO_4\ (aq) + FeSO_4\ (aq) + H_2SO_4\ (aq)$$

(i) Balance the above equation. ***(3 marks)***

$$CuFeS_2\ (s) + 8Fe_2(SO_4)_3\ (s) + 8H_2O\ (l) \longrightarrow CuSO_4\ (aq) + 17FeSO_4\ (aq) + 8H_2SO_4\ (aq)$$

(ii) Describe what you would expect to observe if dil. NaOH (aq) is gradually added to the product mixture until no further change is apparent. Write equations for each reaction occurring, to account for your observations. ***(12 marks)***

- Heat will be evolved due to the strong acid / strong base neutralization reaction occurring between NaOH and H_2SO_4 (2 marks)

$$2NaOH\ (aq) + H_2SO_4\ (aq) \longrightarrow Na_2SO_4\ (aq) + 2H_2O\ (l)\ \ \Delta H = -ve$$

(2 marks)

- The oxidation state if iron in $FeSO_4$ is + 2. A green precipitate will form (2 marks)

$$2NaOH\ (aq) + FeSO_4\ (aq) \longrightarrow Na_2SO_4\ (aq) + Fe(OH)_2\ (s)$$

or

$$Fe^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Fe(OH)_2\ (s)$$

(2 marks)

- A pale blue precipitate will form with $CuSO_4$ (aq) (2 marks)

$$2NaOH\ (aq) + CuSO_4\ (aq) \longrightarrow Na_2SO_4\ (aq) + Cu(OH)_2\ (s)$$

or

$$Cu^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Cu(OH)_2\ (s)$$

(2 marks)

***For consideration**:*

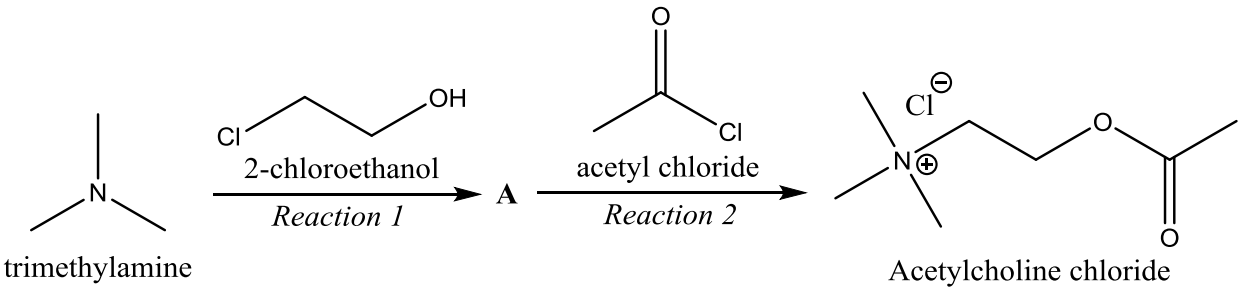
(i) What do you think is the order in which the above three reactions occur?Why?

(ii) Both NH_3 (aq) and NaOH (aq) are alkalis. Why is there a difference in outcome when Cu^{2+} reacts with excess NaOH (aq) vs excess NH_3 (aq)?

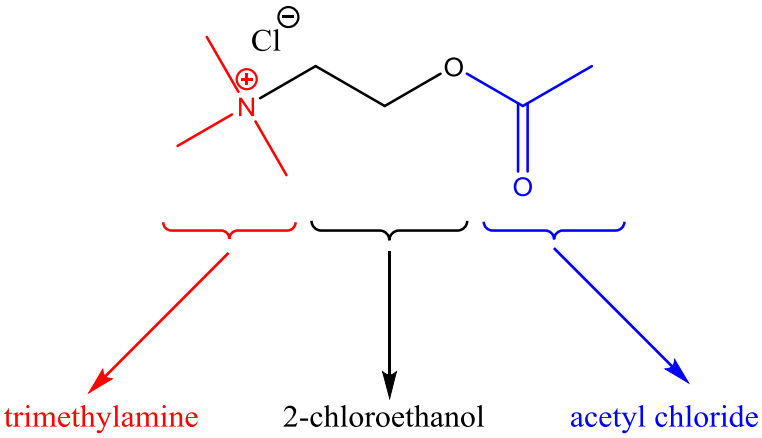
(iii) If left exposed to air, the green precipitate of $Fe(OH)_2$ eventually becomes orange/brown. Why?

3. *The Lionfish (Pterois spp.) is a recent invasive species to the waters of Trinidad and Tobago, with the capacity to cause significant damage to marine life, partly due to its voracious appetite. Furthermore, the presence of venomous spines means that there are few natural predators. The venom is a combination of a neuromuscular toxin (a protein) and a neurotransmitter (acetylcholine).*

Consider a scheme for the synthesis of acetylcholine chloride:

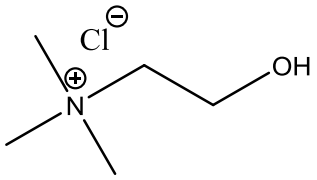


Examine the structure of the final product; one can identify regions corresponding to the various reactants. This strategy (called the "Disconnection Approach") is a powerful technique for synthesizing a given organic compound:



*(a) What is the structure of compound **A**?* ***(2 marks)***

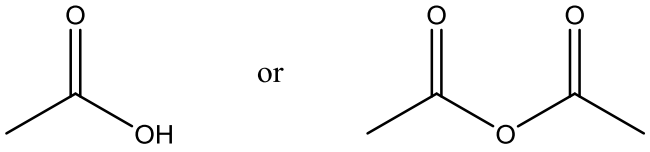
- Trimethylamine is a tertiary amine, and will react with a haloalkane to yield a quaternary ammonium salt:



A

(b) For Reaction 2, suggest another compound that can be used instead of acetyl chloride, to yield the same product. ***(2 marks)***

- Reaction 2 is an esterification reaction: acid chloride + alcohol = ester.
- In place of the acid chloride, the corresponding carboxylic acid, or acid anhydride, may be used:

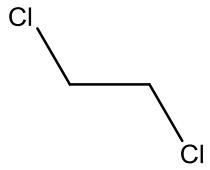


Acetic acid Acetic anhydride

[One student suggested acetyl bromide. This was accepted.]

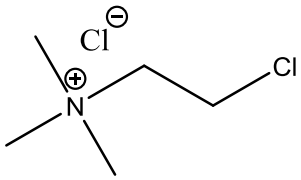
(c) For Reaction 1, if the 2-chloroethanol is replaced with 1,2-dichloroethane, what would be the structure of the product formed? ***(4 marks)***

- 1,2-dichloroethane is an alkyl halide as well:



(2 marks)

- Product:

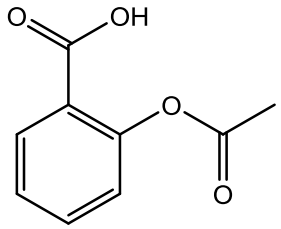


(2 marks)

For consideration*: What is the other organic product that can form? It will be particularly prevalent if the triethylamine is in excess...*

4. *Pain relieving medications are an indispensable feature of modern society, and are diverse in their structure and origin. Some, such as acetylsalicylic acid (commonly known as Aspirin), are derivatives of naturally occurring compounds. The bark of the Willow tree, which contains a precursor of Aspirin (salicylic acid), was used for the treatment of fever and inflammation by the Ancient Egyptians. Others have been identified through a targeted system of drug discovery.*

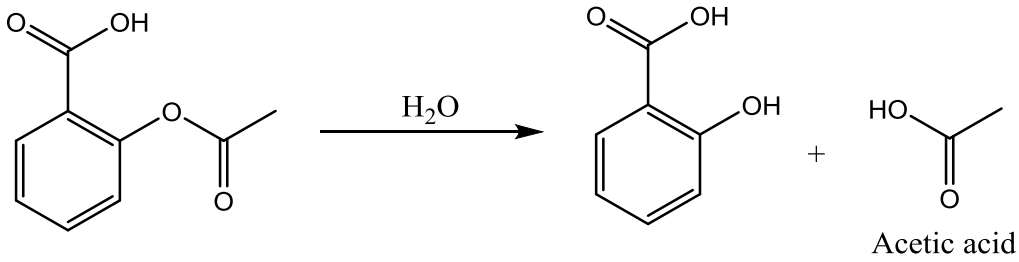
(a) Consider the structure of Aspirin shown below:



Aspirin

Preparations that contain high concentrations of Aspirin, when left exposed to air, eventually begin to smell like vinegar. Suggest a reason for this. ***(3 marks)***

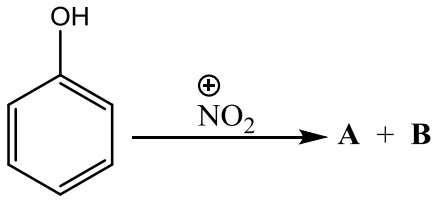
- Vinegar is acetic acid (1 mark)
- The aspirin must be undergoing hydrolysis in the presence of water (from the air) to yield acetic acid (2 marks)



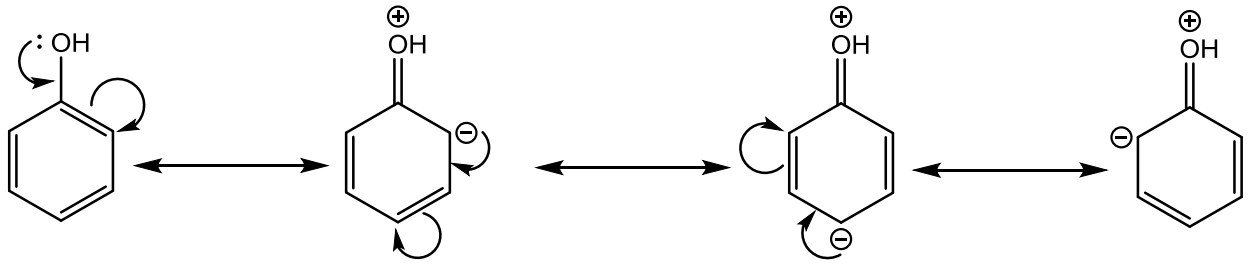
Acetic acid

(Not necessary for marks)

(b) Paracetamol / acetaminophen is marketed under various names - Tylenol, Panadol etc. The first step in its synthesis from phenol, produces two isomers, and can be represented as:

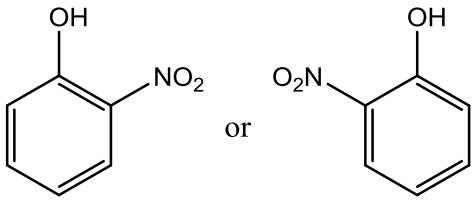


*By examining the partial mechanism for the reaction shown below, suggest identities for **A** and **B**.*

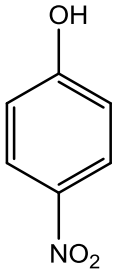


(4 marks)

- Consider where the negative charge is located in the above sequence; these are the points that will attack the positively charged nitronium ion

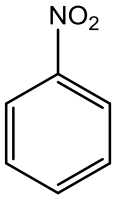


(2 marks)



(2 marks)

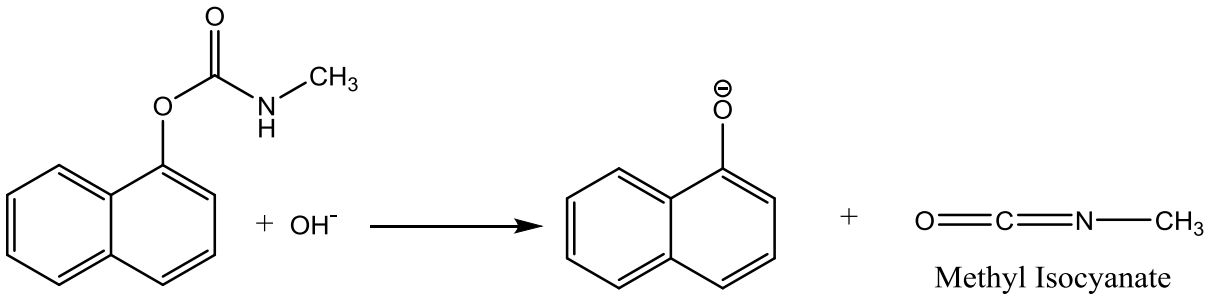
***For consideration**: If the following compound (nitrobenzene) was reacted with the nitronium ion, how would the outcome of the reaction be different, compared to phenol? Why?*



5. *The data presented in this question was taken from the article: Darryl Hawker, **2015**, 92, 1531 - 1535. Kinetics of Carbaryl Hydrolysis: An Undergraduate Environmental Chemistry Laboratory.*

Carbaryl is the first commercially successful pesticide, with the worldwide quantities deployed being greater than that of all other carbamate pesticides. It is commonly known by its trade name, Sevin. Ideally, pesticides should not persist indefinitely in the environment, but rather undergo some transformation to inactive and non-toxic products. One such transformation pathway is hydrolysis, which may occur by either acidic, basic, or enzymatic, mechanisms.

For carbaryl, it has been shown that the acidic mechanism requires too low of a pH (< 5) to be of environmental relevance. The base-mediated hydrolysis occurs at pH > 10, and can be represented as follows:



*Experiments were conducted to determine the rate of base-catalyzed hydrolysis of carbaryl at different pHs. The progress of the reaction was monitored by following the absorbance (A) of carbaryl at a specific wavelength - that corresponding to its maximum absorbance (**Figure 1**)*

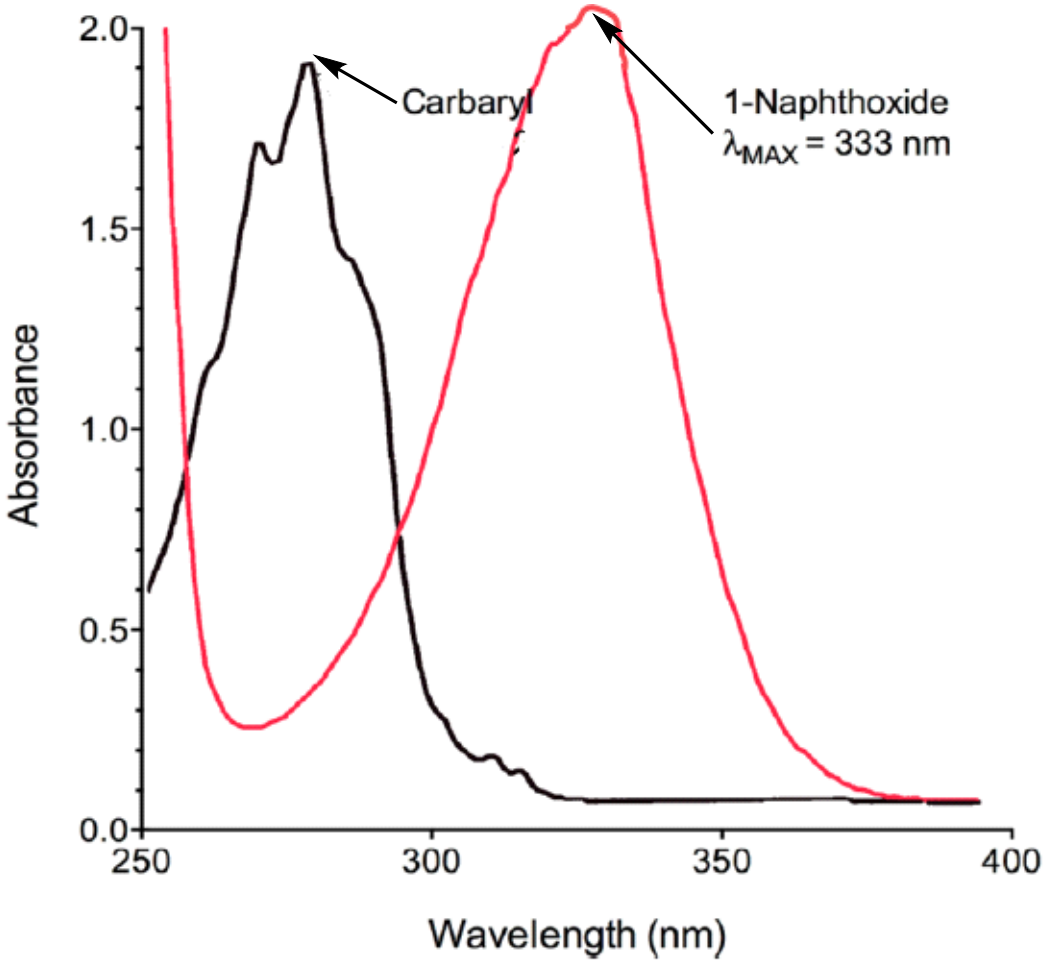


Figure 1: Ultraviolet absorption spectra of carbaryl and 1-naphthoxide

*The concentration of carbaryl, at a given time "t", can be replaced by a corrected absorbance: A_t - A_∞ (Absorbance at time "t" - Absorbance at infinity i.e. when maximum hydrolysis of carbaryl has occurred). Plotting a graph of ln(A_t - A_∞) vs Time will yield a straight line graph. This was done for pHs: 10.0, 10.5, and 11.0 at 20 °C (**Figure 2**).*

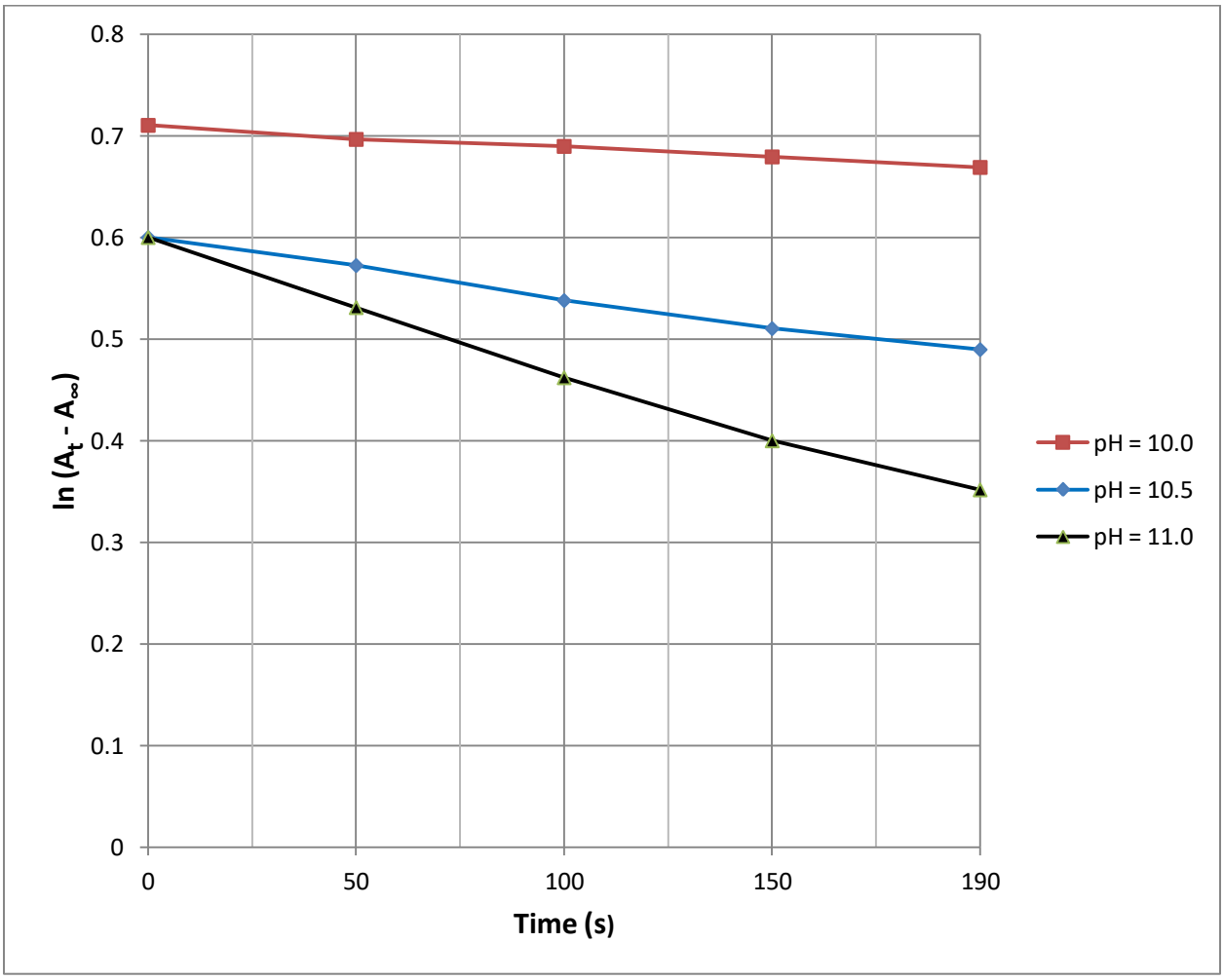
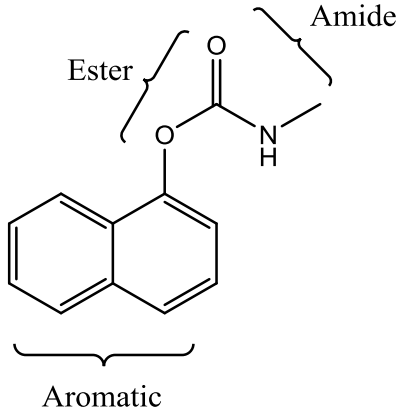


Figure 2: Pseudo-first-order kinetic experiments at different pHs

(a) Identify three (3) functional groups in carbaryl. ***(3 marks)***



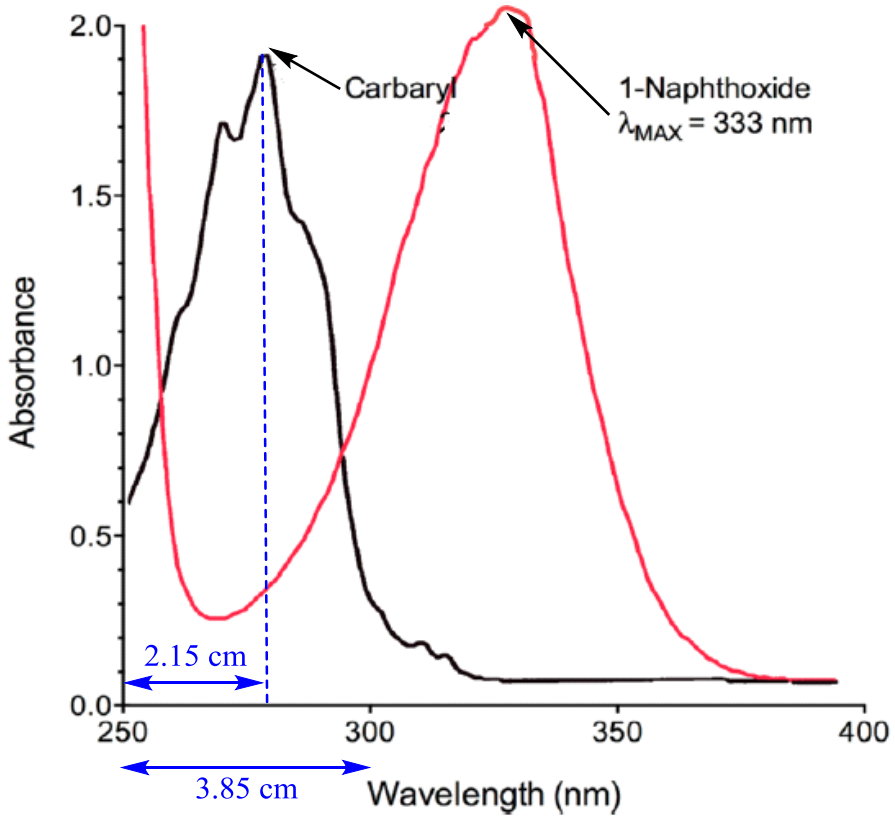
(1 mark) x 3

(b) From ***Figure 1****, calculate the wavelength (λ) at which maximum absorbance of carbaryl occurs.*

As an example, 1-naphthoxide has a λ_{max} *= 333 nm.* ***(5 marks)***

- Identify the point on the x-axis that corresponds to the position of maximum absorbance of carbaryl: 2.1 cm to 2.2 cm (1 mark)
- Identify a suitable distance on the x-axis to determine the scale: 3.8 cm to 3.9 cm = 50 nm (1 mark)
- Therefore: 3.85 cm = 50 nm
  1.00 cm = 13.0 nm
  2.15 cm = 13.0 x 2.15 nm
  = 28.0 nm (1 mark)
- Wavelength of maximum absorbance = Origin point + Increment
  = 250 + 28 (1 mark)
  = 278 nm (1 mark)

- Acceptable range: 276 - 280 nm



*(c) From **Figure 2**, calculate the [H^+] at which there is the highest rate of hydrolysis of carbaryl.*

(6 marks)

- The highest rate of hydrolysis occurs when there is the greatest change in concentration of carbaryl over the period of monitoring. From Figure 2, this occurs when the pH = 11.0 (1 mark)
- pH = - log[H^+] (1 mark)
- - log[H^+] = 11.0 (1 mark)
- log[H^+] = -11.0
- [H^+] = $10^{-11.0}$ (1 mark)

= 1.0 x 10^{-11} moldm^{-3} (1 mark for value; 1 mark for appropriate units)

(*d) In **Figure 2**, the gradient of each individual line = - k' (negative pseudo-first-order rate constant) for that pH. Calculate the value of k' for pH = 11.0* ***(6 marks)***

- Using any two suitable points that are on the straight line: (0, 0.6) and (150, 0.4) (2 marks)
- Gradient = $(y_2 - y_1) / (x_2 - x_1)$ (1 mark)
  = (0.4 - 0.6) / (150 - 0)
  = - 0.0013 (1 mark)
- Gradient = - k'
- k' = - Gradient
  = 0.0013 s^{-1} (1 mark for value; 1 mark for correct units)

(*e) Based on the information presented in this question, do you think carbaryl is a persistent pesticide in the outdoor environment of Trinidad and Tobago? Justify your answer.*

(4 marks)

- In the details, it has been stated that acid-mediated carbaryl degradation requires a low pH not typically found in a general environment. From Figure 2, base-mediated hydrolysis only becomes significant at a pH > 10. It is unlikely that these conditions will exist, apart from contaminated areas (e.g. industrial effluent). (2 marks)
- The data given is for a temperature of 20 °C. Typically, temperatures in Trinidad and Tobago are significantly above this. Increased temperature will increase the rates of reaction. (1 mark)
- It could be that the enzymatic-mediated process is of prominence in the environment. (1 mark)

Give marks for well-reasoned answers.

***For consideration**:*

(i)What is the other isomer of 1-naphthol?

(ii) Which hydroxyl group is more acidic - that of 1-naphthol or phenol? Why?

END OF EXAMINATION PAPER