WATP

CHEMISTRY
UNIT 3 & 4
2020

MARKING GUIDE

Section One: Multiple-choice **(25 marks)**

1	a ☐ b ☐ c ☐ d ■
2	a ☐ b ■ c ☐ d ☐
3	a ☐ b ☐ c ☐ d ■
4	a ☐ b ☐ c ■ d ☐
5	a ☐ b ☐ c ■ d ☐

11	a ☐ b ☐ c ■ d ☐
12	a ☐ b ☐ c ☐ d ■
13	a ■ b ☐ c ☐ d ☐
14	a ☐ b ☐ c ■ d ☐
15	a ☐ b ☐ c ☐ d ■

21	a ☐ b ☐ c ☐ d ■
22	a ☐ b ☐ c ■ d ☐
23	a ☐ b ■ c ☐ d ☐
24	a ☐ b ☐ c ■ d ☐
25	a ☐ b ☐ c ■ d ☐

6	a ☐ b ☐ c ■ d ☐
7	a ☐ b ■ c ☐ d ☐
8	a ■ b ☐ c ☐ d ☐
9	a ■ b ☐ c ☐ d ☐
10	a ■ b ☐ c ☐ d ☐

16	a ☐ b ■ c ☐ d ☐
17	a ■ b ☐ c ☐ d ☐
18	a ■ b ☐ c ☐ d ☐
19	a ☐ b ☐ c ■ d ☐
20	a ☐ b ■ c ☐ d ☐

(1 mark per question)

Section Two: Short answer   **35%   (76 marks)**

This section has **9** questions. Answer **all** questions. Write your answers in the spaces provided.

Supplementary pages for planning/continuing your answers to questions are provided at the end of this Question/Answer booklet. If you use these pages to continue an answer, indicate at the original answer where the answer is continued, i.e. give the page number.

Suggested working time: 60 minutes.

Question 26   **(11 marks)**

Consider 0.05 mol L^{-1} solutions of sodium hydrogencarbonate, potassium hydrogensulfate and lithium phosphate. The table below lists these salts, along with K_c values for the corresponding hydrolysis reactions.

0.05 mol L^{-1} solution	Hydrolysis equation	K_c of hydrolysis reaction
$NaHCO_3(aq)$	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	2.4×10^{-8}
$KHSO_4(aq)$	$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$	1.2×10^{-2}
$Li_3PO_4(aq)$	$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$	2.3×10^{-2}

(a)   Complete the table above, by writing the hydrolysis equation that would take place in each solution.   (3 marks)

(b)   Rank these solutions in order from lowest to highest pH.   (3 marks)

Lowest pH		Highest pH
$KHSO_4$	**$NaHCO_3$**	**Li_3PO_4**

(Allow follow through)

The pH of a lithium carbonate solution, Li_2CO_3(aq), was tested with a pH meter and determined to be 10.3. A chemistry student had 8.50 mL of 0.0500 mol L^{-1} barium hydroxide solution, $Ba(OH)_2$(aq). They wanted to dilute the barium hydroxide so that it would have the same pH as the lithium carbonate solution.

(c)   Calculate the volume of water the student would need to add to the barium hydroxide solution, to produce the same pH as the lithium carbonate.   (5 marks)

In the Li_2CO_3 solution;
$[H^+]$ = 10^{-pH}
                  = $10^{-10.3}$
                  = 5.01187×10^{-11} **mol L^{-1}**   **(1m)**

$[OH^-]$ =   **$(1.0 \times 10^{-14}) / (5.01187 \times 10^{-11})$**
                  = 1.99526×10^{-4} **mol L^{-1}**   **(1m)**

Therefore want;
$c(Ba(OH)_2)$ =   **½ x $[OH^-]$**
                  =   **½ x 1.99526×10^{-4}**
                  = 9.9763×10^{-5} **mol L^{-1}**   **(1m)**

Using $c_1V_1 = c_2V_2$;
V_2   =   **c_1V_1 / c_2**
                  =   **$(0.050 \times 0.0085) / 9.9763 \times 10^{-5}$**
                  =   **4.2601 L**   **(1m)**

$V_2 - V_1$ =   **4.2601 – 0.0085**
                  =   **4.252 L needs to be added**
                  =   **4.25 L   (3 SF)**   **(1m)**

Handwritten note:
$$pOH = 14 - pH$$
$$= 14 - 10.3$$
$$= 3.7$$
$$[OH^-]$$

OR

In the Li_2CO_3 solution;
$[H^+]$ = 10^{-pH}
                  = $10^{-10.3}$
                  = 5.01187×10^{-11} **mol L^{-1}**   **(1m)**

$[OH^-]$ =   **$(1.0 \times 10^{-14}) / (5.01187 \times 10^{-11})$**
                  = 1.99526×10^{-4} **mol L^{-1}**   **(1m)**

In the $Ba(OH)_2$ solution;
$n(Ba(OH)_2)$ =   **cV**
                  =   **0.050 x 0.0085**
                  =   **0.000425 mol**

$n(OH^-)$ =   **2 x $n(Ba(OH)_2)$**
                  =   **0.00085 mol**   **(1m)**

If desired OH^- concentration is 1.99526×10^{-4} mol L^{-1}
$V(OH^-)$ =   **n/c**
                  =   **$0.00085 / 1.99526 \times 10^{-4}$**
                  =   **4.2601 L**   **(1m)**

$V_{final} - V_{inital}$ =   **4.2601 – 0.0085**
                  =   **4.252 L needs to be added**
                  =   **4.25 L   (3 SF)**   **(1m)**

Question 27   **(9 marks)**
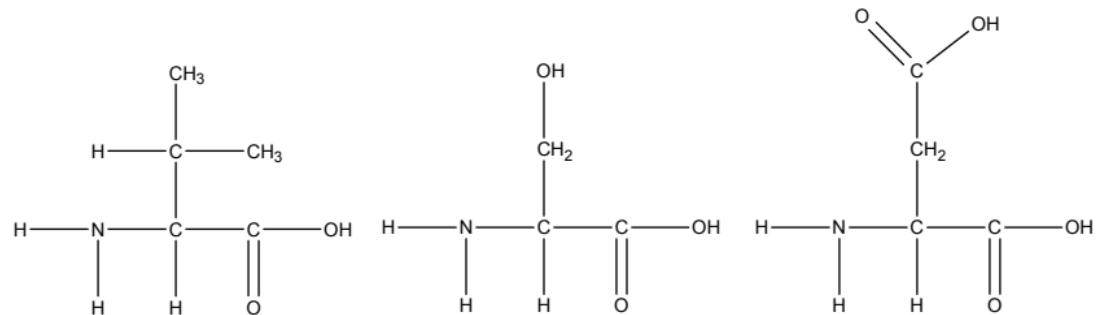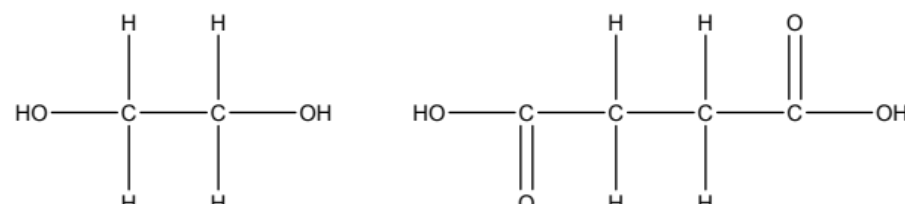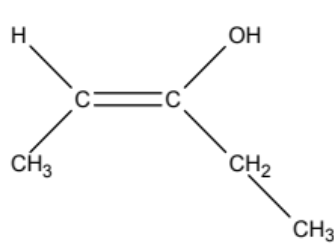
Consider the three (3) different polymer fragments shown below.

A
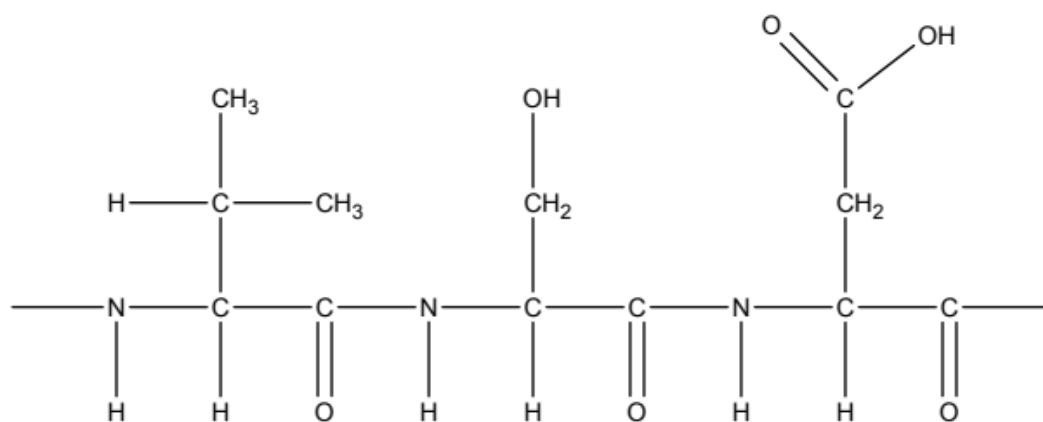
B
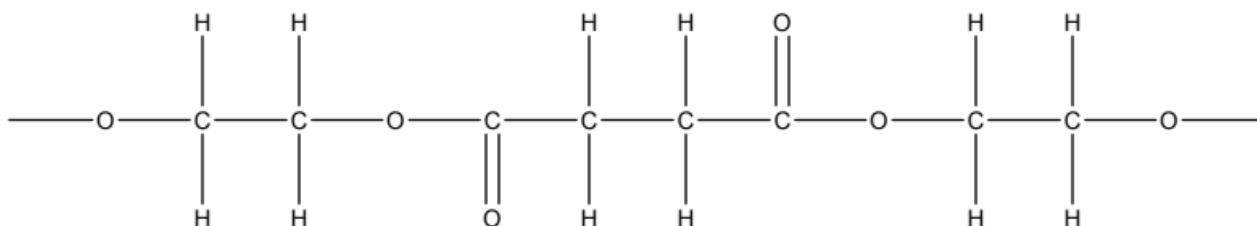
C
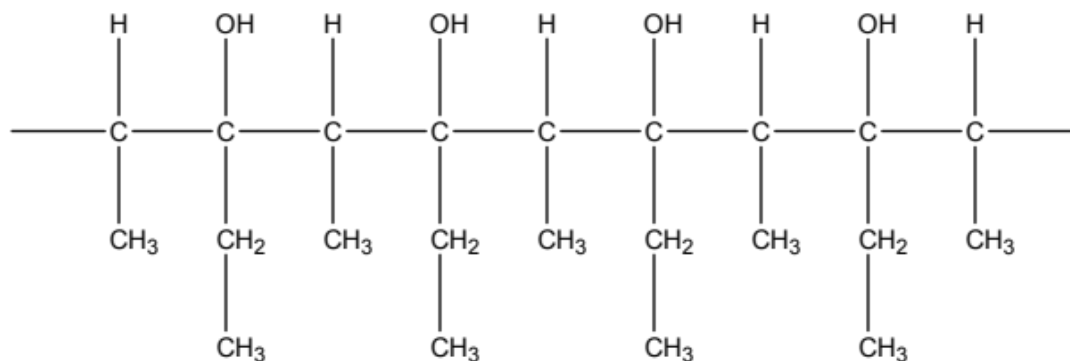
(a)   Classify the polymers as having been formed by addition or condensation polymerisation by writing the letters A, B and C in the appropriate column in the table.   (3 marks)

Addition polymerisation	Condensation polymerisation
C	A B

(b)   Draw the monomer(s) used to form each of these polymers.   (6 marks)

A	 **(3m)** **(-½ once across A, B + C if C not bonded to N and -½ if C not bonded to O)**
B	 **(2m)**
C	 **(1m)**

Question 28   **(10 marks)**

Consider the two redox reactions below.

Reaction A $Sn^{2+}(aq)$ + $2 I^-(aq)$ → $Sn(s)$ + $I_2(aq)$

Reaction B $Sn^{2+}(aq)$ + $Co(s)$ → $Sn(s)$ + $Co^{2+}(aq)$
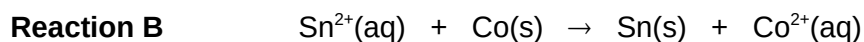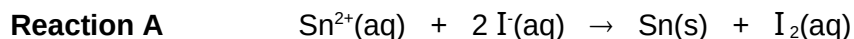
(a)   Which reaction relates to a galvanic cell and which relates to an electrolytic cell? Justify
        your answer.   (3 marks)

        Reaction   **B**   relates to a galvanic cell.

                                                                           (1m)
        Reaction   **A**   relates to an electrolytic cell.

        -     **A is a non-spontaneous reaction / has a negative EMF   (1m)**
        -     **B is spontaneous reaction / has a positive EMF   (1m)**

Using the appropriate reaction (A or B) from above;

(b)   Draw a diagram of the experimental set up that could be used to produce a **galvanic cell**.
        Your diagram should label all the equipment and chemicals required to set up the cell as
        well as showing electron flow. (Note that labels of electrodes, polarity and ion flow are **not**
        required.)   (4 marks)

wire/external circuit

salt bridge
NaNO₃

Co(s)   **Sn(s)**

Co(NO₃)₂(aq)   **Sn(NO₃)₂(aq)**
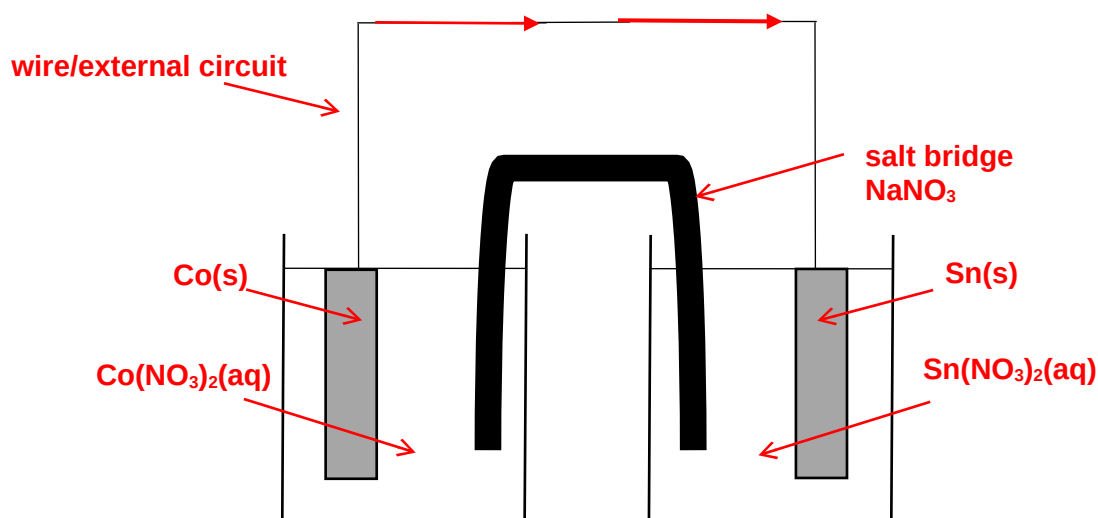
1m Co/Co(NO₃)₂ half-cell

1m Sn/Sn(NO₃)₂ half-cell

1m salt bridge and NaNO₃/KNO₃

1m wire/external circuit and electron flow

(c)   Calculate the EMF produced by this galvanic cell, assuming standard conditions. (1 mark)

EMF   =   - 0.14 + 0.28
**   =   + 0.14 V   (-½ no +, -½ no units, -½ no working)**

Using the appropriate reaction (A or B) on the previous page;

(d)   State the observations for each electrode, if this process was occurring in an **electrolytic cell**. Assume the electrodes are made from graphite.   (2 marks)

positive electrode	**Brown solution forms / colourless solution turns brown**
negative electrode	**Silver metal plates <u>on electrode</u> / silver solid appears (forms) <u>on electrode</u>**

Question 29   **(9 marks)**

A key reaction in the Contact process involves the conversion of sulfur dioxide gas to sulfur trioxide gas. This reversible process can be represented by the equation below.

$$2\ SO_2(g)\ +\ O_2(g)\ \rightleftharpoons\ 2\ SO_3(g)$$
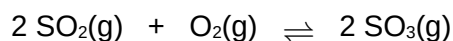
The following graph shows the relationship between temperature and percentage conversion of $SO_2(g)$ to $SO_3(g)$ for this process.
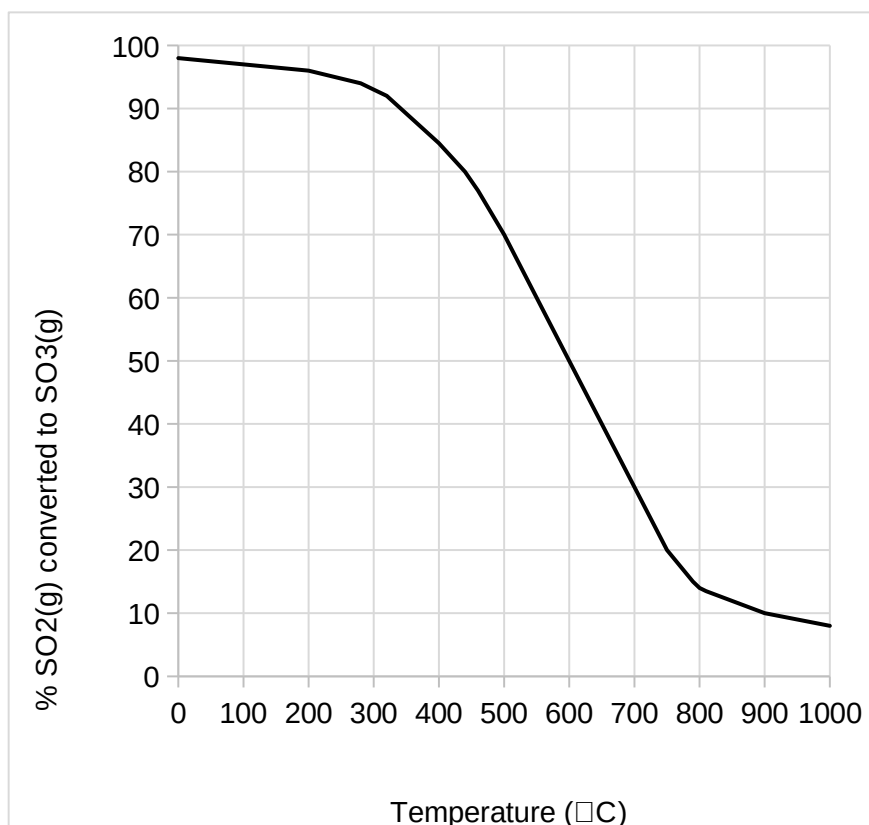
(a)   Use the information in the graph provided to determine if this reaction is endothermic or exothermic as written. Justify your answer.   (3 marks)

- **The graph shows that as temperature is increased this results in a lower SO_3 yield, therefore the reverse reaction is favoured**
- **A temperature increase favours endothermic reaction, so reverse reaction must be endothermic**
- **Therefore, forward reaction/reaction as written, is exothermic**

(b)   Complete the following table, by stating the **pressure** conditions of the system (high or low)
        that would result in;
        (i)   the fastest rate, and
        (ii)   the highest yield.
        Give a brief justification for each of your choices.   (5 marks)

(i) fastest rate	(circle your choice)	**high**	OR	low	**(1m)**
	Justification **Decreased spaces between particles increases frequency of collisions (which increases reaction rate)** 				**(1m)**
(ii) highest yield	(circle your choice)	**high**	OR	low	**(1m)**
	Justification **- A high pressure would increase the rate of both forward and reverse reactions** **- but the forward reaction rate would increase more, causing the reaction to shift to the right (and the yield to increase).** **(2m)**				

When this process is carried out industrially, a low pressure of 1-2 atm is used.

(c)   Suggest a reason for this.   (1 mark)

-     **Save money / high pressure expensive to maintain / safety considerations / the
        increase in reaction rate or yield is possibly not substantial enough to warrant
        using a high pressure… (any relevant suggestion)**

Question 30   **(7 marks)**

Telluric acid has the formula H_6TeO_6. In solid form, it is found as white crystals. These crystals dissolve in water to produce hydronium ions, H_3O^+(aq). The K_a values for telluric acid at 18 °C are given below.

$$K_{a1} \quad = \quad 2.09 \times 10^{-8} \qquad\qquad K_{a2} \quad = \quad 1.00 \times 10^{-11}$$

(a)   Classify telluric acid as strong or weak (circle your choice). Justify your answer.   (2 marks)

strong   OR   **weak**

- **Low K_a value indicates a small degree of ionisation in water / indicates the ratio of ions to molecules in the acid solution is low**

(b)   Label and link the conjugate acid-base pairs in the following equation.   (2 marks)

$$H_6TeO_6(aq) \quad + \quad HPO_4^{2-}(aq) \quad \rightleftharpoons \quad H_2PO_4^-(aq) \quad + \quad H_5TeO_6^-(aq)$$
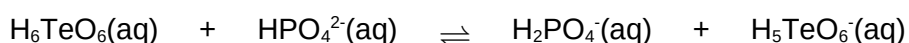
Acid   Base   Conjugate acid   Conjugate base

Telluric acid can be produced by the oxidation of solid tellurium dioxide, TeO_2(s), by hydrogen peroxide solution. In this reaction, hydrogen peroxide forms water.

(c)   Write the oxidation and reduction half-equations and the overall redox equation for this reaction, assuming acidic conditions.   (3 marks)

Oxidation half-equation	**$TeO_2 \; + \; 4\,H_2O \; \rightleftharpoons \; H_6TeO_6 \; + \; 2\,H^+ \; + \; 2\,e^-$**
Reduction half-equation	**$H_2O_2 \; + \; 2\,H^+ \; + \; 2\,e^- \; \rightleftharpoons \; 2\,H_2O$**
Overall redox equation	**$TeO_2 \; + \; H_2O_2 \; + \; 2\,H_2O \; \rightarrow \; H_6TeO_6$**

(-½ no/wrong arrow (once only))

Question 31 **(6 marks)**
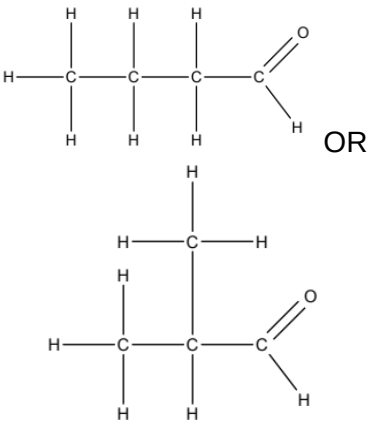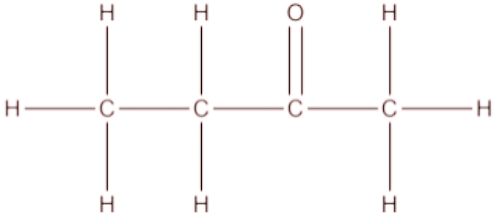
(a) Give the IUPAC names for isomers of $C_3H_6O_2$ matching each description below. (2 marks)

	IUPAC Name
A sweet or fruity smelling liquid	**Methyl ethanoate / ethyl methanoate**
A weak electrolyte with a pH below 7	**Propanoic acid**

(b) Give the IUPAC names for isomers of $C_5H_{12}O$ matching each description below. (2 marks)

	IUPAC Name
A primary alcohol	**Pentan-1-ol / 2-methylbutan-1-ol / 3-methylbutan-1-ol**
A tertiary alcohol	**2-methylbutan-2-ol**

(c) Draw full structural diagrams for isomers of C_4H_8O matching each description below. Include **all** bonds and **all** atoms. (2 marks)

A compound that can be oxidised by acidified $KMnO_4$ solution	A compound that cannot be oxidised by acidified $KMnO_4$ solution
OR	

Accept also appropriate secondary and tertiary cyclic alcohols for (c)

Question 32   **(12 marks)**

The following equilibrium system exists in ocean water and shows the relationship between several of the carbon-species present.

$$Ca^{2+}(aq) \ + \ 2\,HCO_3^-(aq) \ + \ heat \ \rightleftharpoons \ CaCO_3(s) \ + \ H_2O(l) \ + \ CO_2(g)$$
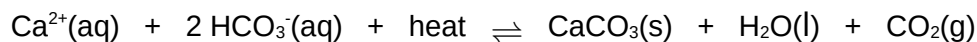
The forward reaction represents the process of '**calcification**', where solid $CaCO_3$ forms. The reverse process represents the '**dissolution**' of solid $CaCO_3$.

(a)   Write the equilibrium constant (K) expression for this system.   (1 mark)

$$K \ = \ \frac{[CO_2]}{[Ca^{2+}]\,[HCO_3^-]^2}$$

The large quantity of $CO_2(g)$ produced and released into our atmosphere by human activity is having an effect on the carbon equilibria in our oceans.

(b)   Explain, in terms of the collision theory and reaction rates, how this increase in the partial pressure of atmospheric $CO_2(g)$ affects the calcification process. Your answer should refer to the equation above.   (3 marks)

- **An increase in partial pressure of CO_2 increases frequency of collisions between CO_2, H_2O and $CaCO_3$ particles (products)**
- **This increase the rate of the reverse reaction relative to the forward reaction**
- **This results in the equilibrium shifting left and reducing the rate of calcification.**

(c)   State two (2) consequences for calcifying species that may result from this increase in the partial pressure of atmospheric CO_2(g).   (2 marks)

-    **Decreased ability to form shells or exoskeleton / disintegration of existing shells, corals or reefs / habitat destruction / extinction or endangerment of species / disruption of food webs… (any 2 relevant statements)**

(d)   Write a three-step reaction sequence, showing how an increased partial pressure of atmospheric CO_2(g) leads to a decrease in ocean pH.   (3 marks)

OR

Step 1	$CO_2(g) \rightleftharpoons CO_2(aq)$	$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
Step 2	$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
Step 3	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

An artificial replica of this equilibrium system was set up in a closed container, which was sealed with a moveable plunger, allowing for variable gas volume and pressure to be achieved. The set up is illustrated in the diagram to the right.

plunger
CO_2(g)
H_2O(l), HCO_3^-(aq), Ca^{2+}(aq)
$CaCO_3$(s)
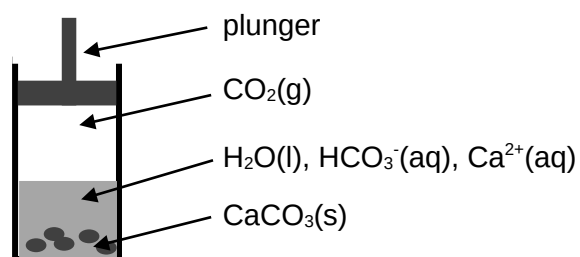
(e)   Consider the effect of imposing the following changes on the system. Complete the table below by stating whether the process of calcification or dissolution, or neither, is favoured.
                                                                                                    (3 marks)

	Favoured process (calcification / dissolution / neither)
The volume of the system is decreased by pushing the plunger down	**Dissolution**
Additional $CaCO_3$(s) is added to the system	**Neither**
The temperature of the system is increased	**Calcification**

Question 33   **(6 marks)**

Consider the distinguishing chemical tests described below.

(a)   Write **observations** for the following test, which can be used to distinguish between
        solutions of sodium chloride and sodium iodide.   (2 marks)

	Bromine water, $Br_2(aq)$, is added to each
NaCl(aq)	**Orange and colourless solutions mixed, no observed change**
NaI(aq)	**Orange and colourless solutions mixed, brown solution forms**

(b)   Write an **ionic equation**, or state 'no observable change', for the following test which can
        be used to distinguish between solutions of silver nitrate and zinc sulfate.   (3 marks)

	A piece of nickel metal, Ni(s), is added to each
$AgNO_3$(aq)	**2 Ag$^+$(aq) + Ni(s) → 2 Ag(s) + Ni^{2+}(aq) (2m)**
$ZnSO_4$(aq)	**No observable change (1m)**

(c)   Name or give the formula of a substance that could be added to each solution, to produce
        the observations given for the following distinguishing test.   (1 mark)

	Substance added: **NaHCO$_3$(s) / Na$_2$CO$_3$(s) / KHCO$_3$(s)… etc**
HCHO(aq)	White powder mixed with colourless solution. No changes are observed.
HCOOH(aq)	White powder mixed with colourless solution. White powder dissolves and colourless, odourless gas is produced.

Question 34   **(6 marks)**

Benzoic acid is found in many berries and some other fruits, and is used as a food preservative. The structure of benzoic acid is shown below. In an aqueous environment, benzoic acid ionises and exists in equilibrium with the benzoate ion.
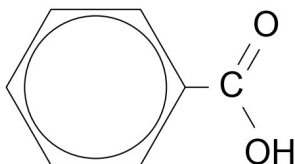
(a)   Write the equation for the reaction between benzoic acid and water. Show all atoms.

(1 mark)

(b) The ease with which a substance is excreted from the body is determined in part by its solubility in water. Is benzoic acid more or less miscible with water than acetic (ethanoic) acid, and hence more or less readily excreted from the body? Explain, in detail, your choice.   (5 marks)

- Benzoic acid is less miscible in water than acetic acid.

- Both substances contain dispersion forces, dipole-dipole forces and hydrogen bonding (the dispersion forces in benzoic acid are more significant than in acetic acid).

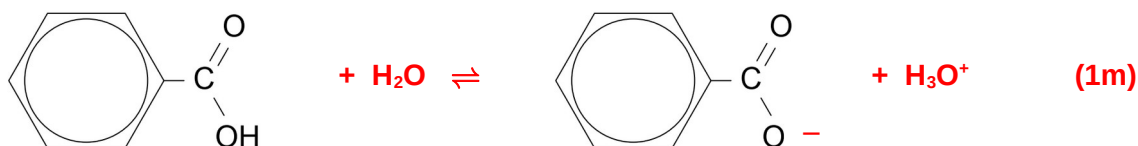**- When acetic acid dissolves in water the hydrogen bonding/ion dipoles between the water and acetic acid molecules are greater in strength than the intermolecular forces between the acetic acid molecules and the hydrogen bonding between the water molecules.**

- When benzoic acid dissolves in water the hydrogen bonding/ion dipoles between the water and benzoic acid molecules are greater in strength than the intermolecular forces between the acetic acid molecules and the hydrogen bonding between the water molecules

- but as the dispersion forces in benzoic acid are more significant, it is less soluble in water than acetic acid.

End of Section Two

Section Three: Extended answer   **40%   (97 marks)**

This section contains **six (6)** questions. You must answer **all** questions. Write your answers in the spaces provided below.

Where questions require an explanation and/or description, marks are awarded for the relevant chemical content and also for coherence and clarity of expression. Lists or dot points are unlikely to gain full marks.

Final answers to calculations should be expressed to the appropriate number of significant figures.

Supplementary pages for planning/continuing your answers to questions are provided at the end of this Question/Answer booklet. If you use these pages to continue an answer, indicate at the original answer where the answer is continued, i.e. give the page number.

Suggested working time: 70 minutes.

Question 35   **(18 marks)**

The following reversible reaction between chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) was set up in a beaker and allowed to establish equilibrium. The initial colour of the equilibrium system was a light orange. The equilibrium can be represented by the following equation;

$$2\ CrO_4^{2-}(aq)\ +\ 2\ H^+(aq)\ \rightleftharpoons\ Cr_2O_7^{2-}(aq)\ +\ H_2O(l)$$
$$\textit{yellow}\qquad\qquad\qquad\qquad\textit{orange}$$
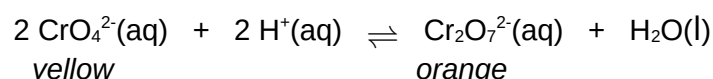
This equilibrium system is 'pH dependent'.

(a)   Complete the following table, by writing the colour this equilibrium system would appear at both a low and a high pH.   (1 mark)

Colour at low pH	Colour at high pH
orange	**yellow**

The equilibrium mixture was then divided equally into 2 smaller beakers. The separate beakers, Beaker 1 and Beaker 2, were treated as described below.

Beaker 1

- 10 drops of 2 mol L^{-1} HCl(aq) were added at Time T1, and equilibrium was re-established at Time E2.

You may assume the increase in volume due to the added HCl(aq) is negligible.

The following graph represents the equilibrium in Beaker 1.

$$2 \, CrO_4^{2-}(aq) \;+\; 2 \, H^+(aq) \;\rightleftharpoons\; Cr_2O_7^{2-}(aq) \;+\; H_2O(l)$$
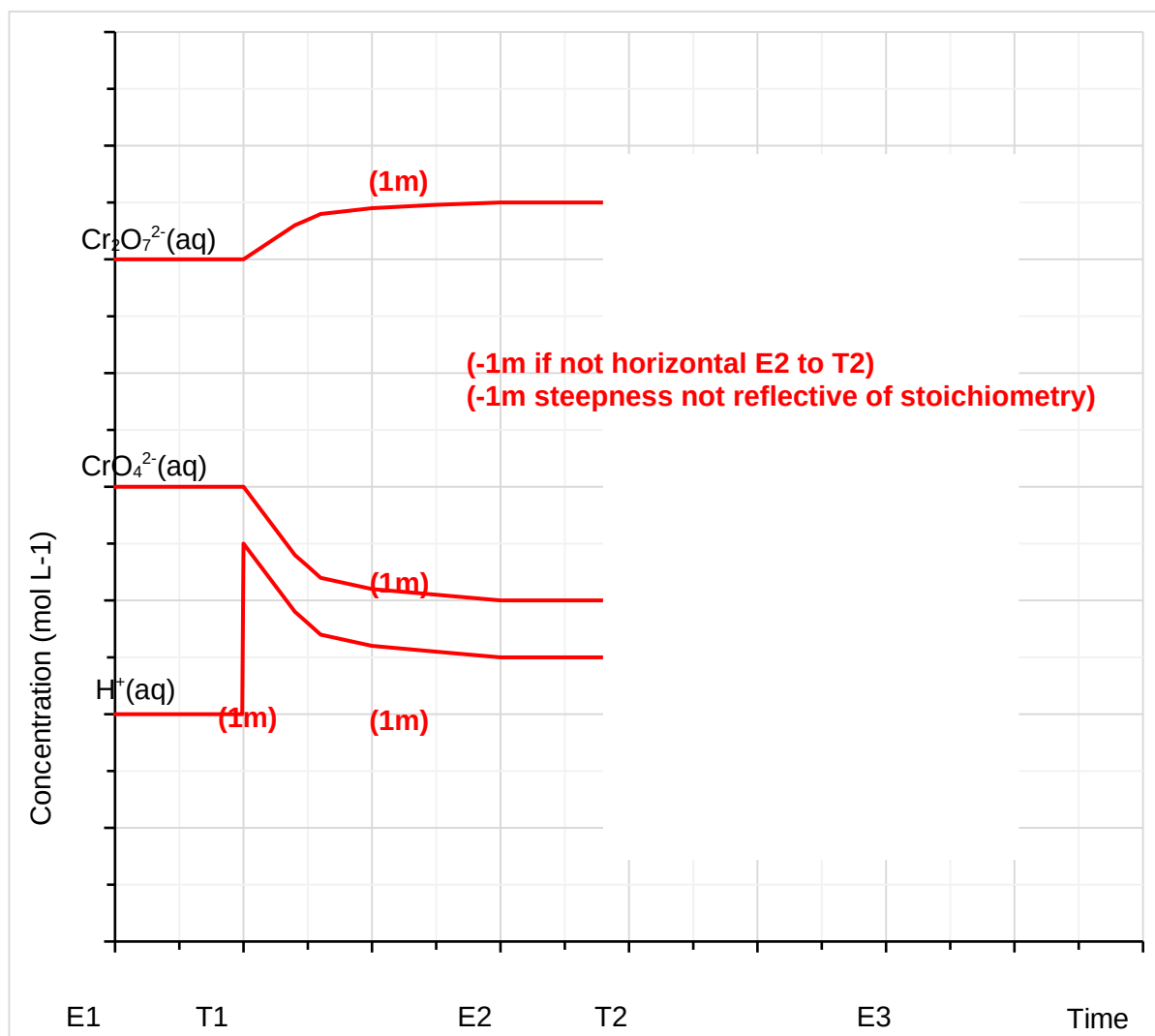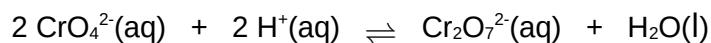
(b)   Plot the concentration for each of the ions shown on the graph, from Time T1 to Time T2.

(4 marks)

-

Beaker 2

The following graph represents the equilibrium in Beaker 2.

$$2 \ CrO_4^{2-}(aq) \ + \ 2 \ H^+(aq) \ \rightleftharpoons \ Cr_2O_7^{2-}(aq) \ + \ H_2O(l)$$
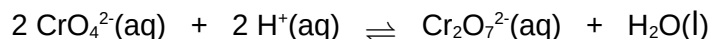
The volume of the solution in Beaker 2 was doubled by adding some distilled water at Time T1 and equilibrium was re-established at Time T2.
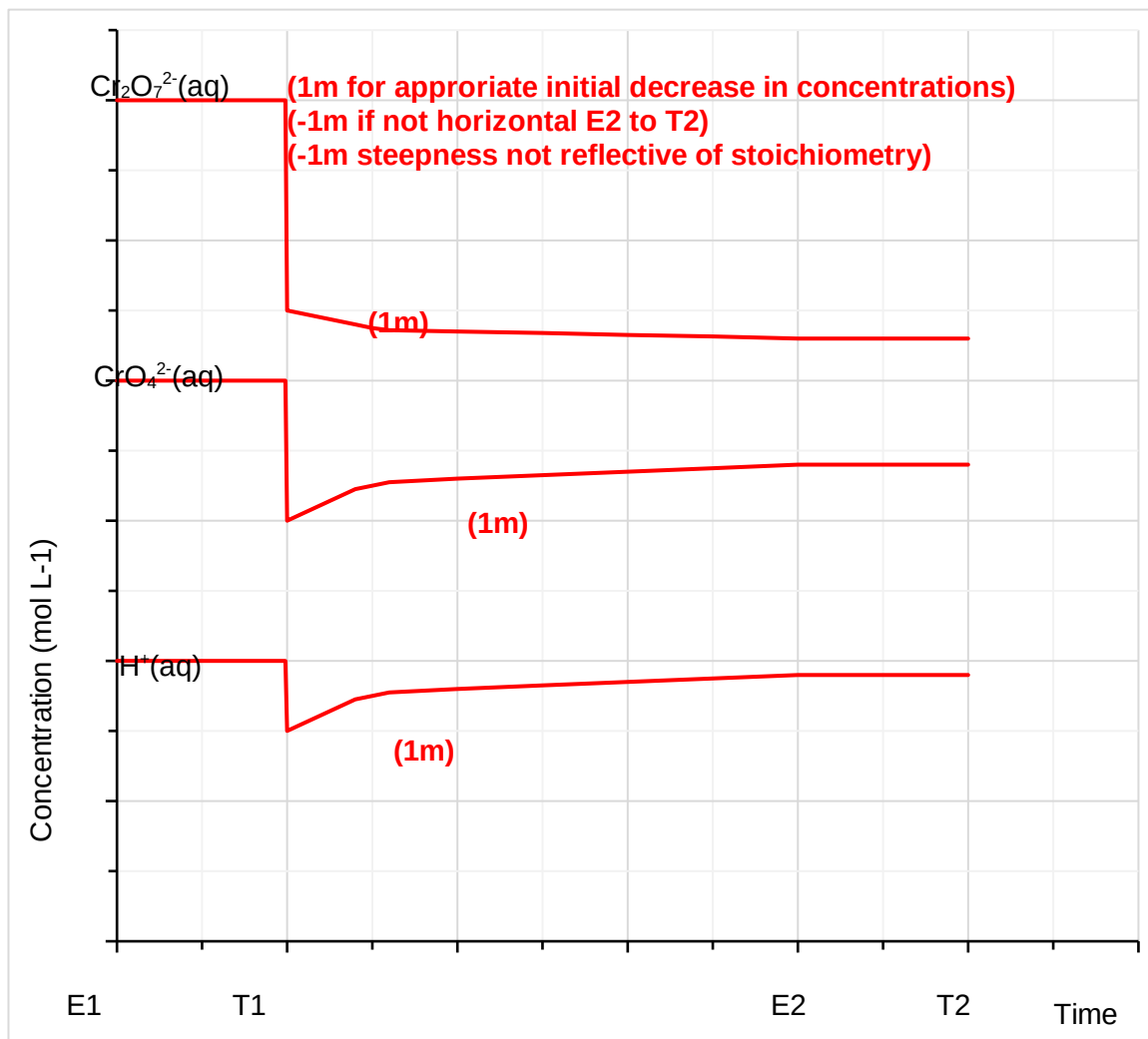
(c)   Plot the concentration for each of the ions shown on the graph, from Time T1 to Time T2.
(4 marks)

(d)   Justify the equilibrium shift in Beaker 2 using Le Chatelier's Principle.   (3 marks)

- Le Chatelier's Principle states if a system at equilibrium is subjected to a change, the equilibrium will shift to partially counteract the imposed change.
- Since all aqueous species are diluted, system favours direction which produces the greatest increase in concentration (number of aqueous species)
- Ratio of aqueous species is 4:1/more particles are produced through the reverse reaction therefore the reverse reaction is favoured/equilibrium shifts left

At Time T2, Beaker 2 was placed into an ice bath. Over several minutes, the equilibrium became a more yellow colour.

(e)   Explain what information this provides about the heat of reaction (H) for this equilibrium
       system.   (3 marks)

-    **A more yellow colour indicates [CrO_4^{2-}] increased.**
-    **As temperature was decreased, equilibrium shifts to increase the temperature and favours the exothermic reaction**
-    **Therefore the reverse reaction is exothermic and the forward reaction (as written) is endothermic, i.e. H is positive**

(f)   Complete the reaction rate graph below, for both the forward and reverse reaction rates,
       from Time T2 until the re-establishment of equilibrium at Time E3.   (3 marks)
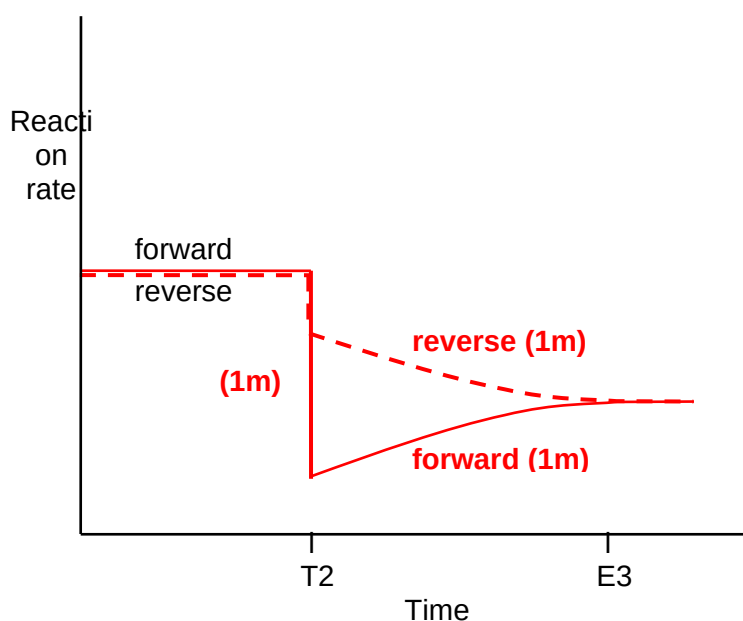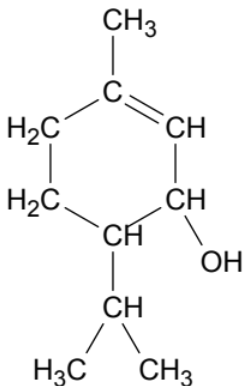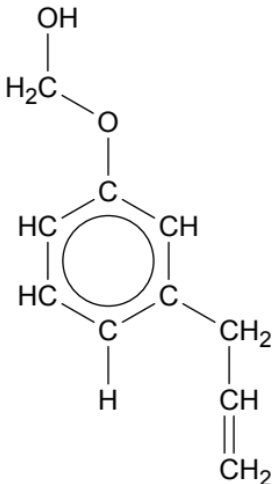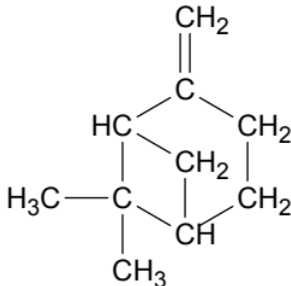
Question 36   **(15 marks)**

In traditional Aboriginal culture, native plants have been used for many generations to treat or heal those who are sick or injured. Research is now being carried out on many of the various plants that were used by Aboriginal peoples and has found that they often contain well known anti-bacterial or anti-inflammatory compounds.

The table below gives information on three (3) compounds that have been identified in native Australian plants which were used by Aboriginal peoples to treat various medical conditions.

Name of compound	Terpinenol	Eugenol	Pinene
Extracted from	Tea tree oil	Australian lemongrass	Eucalyptus oil
Aboriginal medicinal use	treating wounds and throat ailments	treating headaches, colds and muscle pain	treating body pain, fever and chills
Structure			

A chemist was given a pure sample of each of these 3 compounds for analysis. However, the samples were not labelled.

(a)   Explain why the addition of bromine water to each of these samples would **not** be a useful distinguishing test.   (2 marks)

- **All substances have a carbon-carbon double bond/ alkene functional group**
- **Therefore all would undergo addition reactions and decolourise bromine water**

The compound 'pinene' could quickly be distinguished from the other two compounds by adding a few drops of acidified sodium dichromate solution to each.

(b)   Justify how this test would allow for the identification of pinene, including relevant observations in your answer. (Note that equations are **not** required.)   (3 marks)

-     **Pinene would not react / be oxidised whilst the other two compounds would**
-     **Pinene sample would remain orange in colour**
-     **Other two compounds would turn from orange to deep green**

The chemist then used combustion analysis to distinguish 'terpinenol' and 'eugenol'. A 7.58 g sample of one of the compounds was taken for analysis. Upon combustion, 20.33 g of carbon dioxide and 4.99 g of water vapour was produced.

(c)   Determine the empirical formula of this sample and identify which compound was being analysed.   (8 marks)

$n(CO_2)$ =   **20.33 /44.01**
            =   **0.461940468 mol = n(C)   (1m)**

$n(H_2O)$ =   **4.99/18.016**
            =   **0.276976021 mol**
$n(H)$ =   **2 x 0.276976021**
            =   **0.553952042 mol   (1m)**

$m(O)$ =   **7.58 – ((0.461940468 x 12.01)+(0.553952042 x 1.008))**
            =   **7.58 – 6.10628868**
            =   **1.47371132 g**
$n(O)$ =   **1.47371132/16.00**
            =   **0.092106957 mol   (1m)**
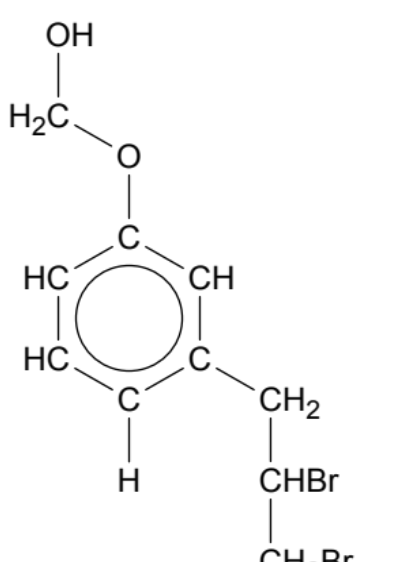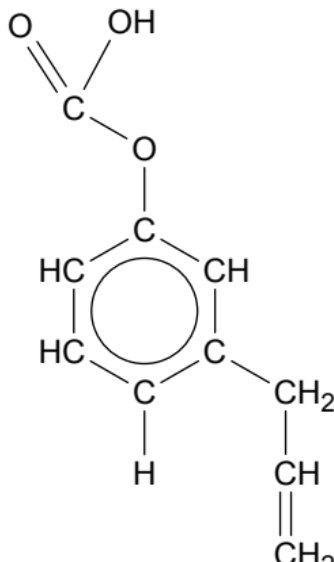
	C	H	O	
n	0.461940468	0.553952042	0.092106957	**(1m)**
ratio	0.461940468 / 0.092106957 = 5.02	0.553952042 / 0.092106957 = 6.01	0.092106957 / 0.092106957 = 1.00	**(1m)**
round	5	6	1	

Therefore EF is C_5H_6O (1m)

Substance is 'eugenol' (1m)
as the MF is 2 x this EF (1m)
(MF of terpinenol does not match this EF)

The chemist then carried out two further chemical tests with the compound identified by combustion analysis in part (c).

(d)   Draw structural diagrams (showing all atoms) for the resulting organic compound formed when the substance identified in (c) reacts
         (i)   with bromine water
         (ii)   with acidified sodium dichromate.   (2 marks)

	bromine water, Br_2(aq)	chemical test described in part (b)
Organic product formed		

- **If students incorrectly say 'terpinenol' was identified in part (b), award full marks if their answers in part (c) use terpinenol correctly**

Question 37 **(13 marks)**

A beaker contained 135 mL of 2.73 mol L^{-1} hydrochloric acid, HCl(aq). A group of chemistry students were given some 1.98 mol L^{-1} ammonia solution, NH$_3$(aq), and asked to neutralise the acid.

They measured 344 mL of the ammonia solution and poured it into the beaker containing the hydrochloric acid. The equation for the reaction that took place is given below.

$$HCl(aq) \ + \ NH_3(aq) \ \rightarrow \ NH_4Cl(aq)$$
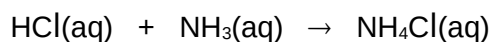
(a)   Calculate the final concentration, in mol L^{-1}, of any excess reagent present.   (5 marks)

n(HCl) **=** **cV**   **n(NH$_3$)** **=** **cV**
        = **2.73 x 0.135**   **=** **1.98 x 0.344**
        = **0.36855 mol**   **=** **0.68112 mol**

mole to mole comparison
n(HCl) **=** **n(HCl)/1**   **n(NH$_3$)** **=** **n(NH$_3$)/1**
        = **0.36855 mol**   **=** **0.68112 mol** **(1m)**

Therefore HCl is limiting reagent as it is present less on a mole-to-mole basis. **(1m)**

n(NH$_3$)$_{reacted}$ **=** **1 x n(HCl)**
        = **0.36855 mol** **(1m)**

n(NH$_3$)$_{xs}$ **=** **0.68122 – 0.36855**
        = **0.31257 mol** **(1m)**

c(NH$_3$) **=** **n/V**
        = **0.31257 / 0.479**
        = **0.65255 mol L^{-1}**
        = **6.53 x 10^{-1} mol L^{-1} (3 SF) (1m)**

(b)   Calculate the final concentration, in mol L^{-1}, of ammonium chloride product.   (2 marks)

n(NH$_4$Cl)   =   n(HCl)
**   =   0.36855 mol   (1m)**

c(NH$_4$Cl)   =   n/V
**   =   0.36855 / 0.479**
**   =   0.769415 mol L^{-1}**
**   =   7.69 x 10^{-1} mol L^{-1} (3 SF) (1m)**

One of the chemistry students in the group proposed that the final mixture in the beaker would act as a buffer solution.

(c)   Was this student correct? Justify your answer using relevant chemical theory. Include a
         brief description of how the student's hypothesis could be tested experimentally.   (6 marks)

-   **Yes the solution can act as a buffer**
-   **The solution contains a weak base (NH$_3$(aq)) and its conjugate acid (NH$_4^+$(aq)), (a conjugate acid-base pair) with similar and high concentrations of each component**
-   **The solution can therefore act as a buffer by resisting a change in pH upon the addition of small amounts of H$_3$O$^+$ or OH$^-$**

    To test experimentally:
-   **Separate the mixture into 2 beakers and measure the initial pH**
-   **Add a small amount of strong acid to one and a small amount of strong base to the other, measure the resulting pH**
-   **If no significant change in pH then solution is buffering**

    (Note: if students get the calculations incorrect, and then argue against the final mixture acting as a buffer based on their answers, follow through marks may be awarded as appropriate.)

Question 38   **(25 marks)**

An ongoing area of chemical research relates to the optimisation of biodiesel production from the triglycerides in waste vegetable oil. The chemical process involves converting waste vegetable oil into biodiesel, in a reaction catalysed by sodium hydroxide (NaOH). A common component found in waste vegetable oil is the triglyceride 'triolein'. The structure of triolein is shown below.
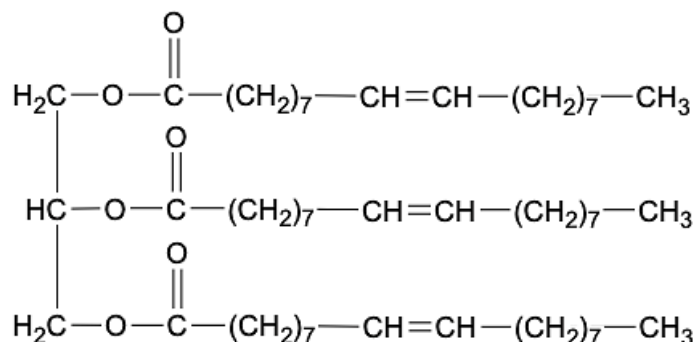
(a)   What is biodiesel? Describe how triolein can be converted into biodiesel, by naming the chemical reaction and stating the additional reactant required.   (3 marks)

- **Biodiesel is a biofuel (with similar uses to diesel) produced from biomass feedstocks (renewable resources)/Biodiesel is a long chain methyl or ethyl ester**
- **Made through transesterification**
- **when reacted with methanol (or ethanol / propanol)**

One of the problems associated with converting waste vegetable oil into biodiesel, is that the vegetable oil can often contain a high levels of free fatty acids (FFAs). In the case of triolein, when heated for use in cooking it can produce 'oleic acid', $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$.

The 'percent free fatty acid' (% FFA) of vegetable oil is calculated as the grams of FFA present per 100 g of oil. The concentration of FFA in any oil, is generally calculated and stated in terms of 'oleic acid', as this is a common fatty acid of average molecular weight.

i.e.   % FFA   = $\dfrac{m(oleic\ acid)}{m(oil)}$ x   100

When making biodiesel, if the waste vegetable oil contains greater than 1% FFA by mass, extra sodium hydroxide must be added to the reaction mix. This ensures that the FFAs are completely neutralised, and that there is still enough sodium hydroxide left over to act as a catalyst in the formation of biodiesel.

(b)   Write the equation for the reaction of oleic acid with sodium hydroxide.   (2 marks)

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH + OH^- \rightarrow CH_3(CH_2)_7CH=CH(CH_2)_7COO^- + H_2O$
(**must** show structural representation of COOH/COO$^-$)

OR

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH + NaOH \rightarrow CH_3(CH_2)_7CH=CH(CH_2)_7COO^-Na^+ + H_2O$
(**must** show structural representation of COOH/COO$^-$)
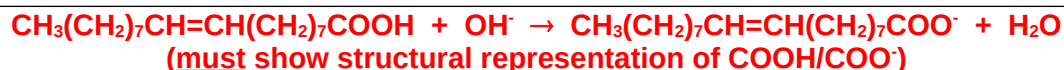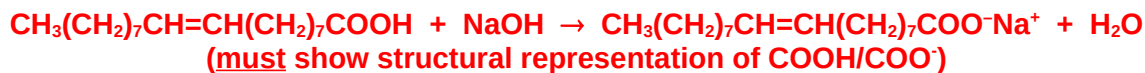
(c)   Give the **general** name for the type of organic substance produced in (b).   (1 mark)

-     **soap**

A particular batch of waste vegetable oil from a restaurant was being analysed for FFA content, before being converted into biodiesel. The amount of sodium hydroxide required to neutralise the FFAs present in a sample of waste vegetable oil is determined by titration.

A 10.00 mL sample of the waste vegetable oil was taken and mixed with 100.0 mL of propan-2-ol. 15.00 mL aliquots of the diluted oil were then titrated against 0.01180 mol L^{-1} NaOH(aq). This required an average titre of 10.66 mL. The density of the waste vegetable oil was 0.8950 g mL^{-1}.

(d)   Calculate the % FFA in this batch of waste vegetable oil.   (6 marks)
         (The molecular mass of oleic acid is 282.452 g mol^{-1}.)

$n(NaOH)$ = cV
                 =   0.01180 x 0.01066
                 =   1.25788 x 10^{-4} mol   (1m)

$n(oleic\ in\ 15\ mL)$ =   1.25788 x 10^{-4} mol   (1m)

$n(oleic\ in\ 110\ mL)$ =   1.25788 x 10^{-4} x (110/15)
                             =   9.22445 x 10^{-4} mol   (1m)
                             = $n(oleic\ in\ 10\ mL\ sample)$

$m(oleic)$ = nM
                 =   9.22445 x 10^{-4} x 282.452
                 =   0.260547 g   (1m)

 = m / V, therefore
$m(oil)$ = V
                 =   0.895 x 10
                 =   8.95 g   (1m)

% FFAs   =   m(oleic) / m(oil) x 100
               =   0.260547 / 8.95 x 100
               =   2.9111 %
               =   2.911 %   (4 SF)   (1m)

(e)   State two (2) reasons for performing repeat trials in a titration, in order to obtain an average titre. (2 marks)

- **To improve reliability / to minimise <u>random</u> error / so an average can be calculated… (any 2 relevant statements)**

(f)   If the burette had been rinsed with water before use in this titration, state the effect this would have had on the calculated % FFA content. Justify your answer. (2 marks)

- **This would dilute the NaOH(aq) so a larger titre volume would be required to reach the equivalence point**
- **This would give a higher calculated % FFA content**

The standard amount of solid sodium hydroxide catalyst, NaOH(s), added to the reaction mix during biodiesel production, is 3.50 g per litre of vegetable oil, **plus** any extra NaOH that is required to neutralise the FFAs present.

A 2500.0 L batch of the waste oil from the restaurant was to be converted to biodiesel.

(g)   Calculate the total mass of NaOH needed for this reaction mixture. (5 marks)

m(NaOH required as catalyst for 2500 L oil)   =   3.5 x 2500
**   =   8750 g   (1m)**
from part (d)
n(NaOH to neutralise FFAs in 10 mL oil)   =   n(oleic in 10 mL)
**   = 9.22445×10^{-4} mol   (1m)**
n(NaOH to neutralise 2500 L oil)   = 9.22445×10^{-4} x (2500/0.010)
**   =   230.61125 mol   (1m)**
m(NaOH to neutralise 2500 L oil)   =   nM
**   =   230.61125 x 39.998**
**   =   9223.9888 g   (1m)**
m(NaOH required in total for 2500 L)   =   8750 + 9223.9888
**   =   17974 g**
**   = 1.80×10^{4} g   (3 SF)   (1m)**

OR

m(FFA) in 10 mL   =   0.26 g
m(FFA) in 2500 L   =   (0.26/0.010) x 2500
**   =   65136.6 g   (1m)**
n(FFA)   =   (65136.6/282.452)
**   =   230.6 mol   (1m)**
n(NaOH)$_{FFA}$ =   n(FFA)
**   =   230.6 mol**
m(NaOH)$_{FFA}$ =   230.6 x 39.998
**   =   9223.99 g   (1m)**
m(NaOH)$_{oil}$ =   3.5 x 2500
**   =   8750 g   (1m)**
m(NaOH)$_{T}$ =   8750 + 9223.99
**   = 1.80×10^{4} g   (3 SF)   (1m)**

An alternate catalyst for the production of biodiesel by this method, is the enzyme lipase.

(h)   State **two (2)** similarities and **two (2)** differences in the way the NaOH and lipase catalysts
   function in this process.   (4 marks)

Similarities	
1	**- Both increase reaction rate** **- Both provide alternate reaction pathway with a lower activation energy** **- Both catalysts are the same at the end of the reaction as they were at the beginning of the reaction**
2	**(any 2)**

Differences	
1	**- Lipase is a biological catalyst / protein , NaOH is an inorganic substance** **- Lipase is temperature / pH sensitive, NaOH is not** **- Lipase work by a 'lock and key' mechanism / are reagent specific, NaOH is not reagent specific** **- Lipase specificity doesn't cause unwanted side reactions, NaOH can**
2	**- Lipase can simultaneously cause transesterification and esterification of FFA, NaOH can only cause transesterification** **- Lipase is made ineffective by excess methanol, NaOH is not** **- Lipase is very expensive, NaOH is relatively cheap** **- Lipase is difficult to extract at the end, NaOH is not** **- NaOH is caustic at high concentrations, lipase is not** **(any 2)**

(Differences must <u>discuss both</u> lipase and NaOH to be awarded one mark)

Question 39 **(18 marks)**

With an emphasis on the principles of green chemistry becoming essential in our modern world, this has led to many new areas of research. One particular type of fuel cell, the 'high temperature carbonate fuel cell' has been designed so that it can be powered by biogas (a mixture of methane and carbon dioxide gases).

High temperature carbonate fuel cells are often built at landfill sites, where biogas is already being produced. As microbes digest organic waste, they produce methane in a process called 'methanogenesis'. This is performed by bacteria called methanogens, which convert the glucose found in landfill into biogas.

> *Step 1*: $C_6H_{12}O_6(s) \rightarrow 3\ CO_2(g) + 3\ CH_4(g)$
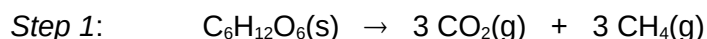
The carbon dioxide is removed from the biogas and the methane is then used in the carbonate fuel cell, where it reacts with water to produce hydrogen gas.

> *Step 2*: $CH_4(g) + H_2O(g) \rightarrow 3\ H_2(g) + CO(g)$
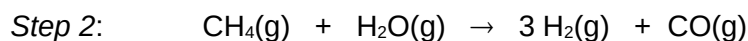
The hydrogen gas is then reacted with oxygen gas in the fuel cell to produce electrical energy.

> *Step 3*: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
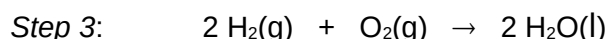
The process of methanogenesis (i.e. Step 1) is catalysed by various enzymes (proteins) present in the bacteria. These enzymes are sensitive to both temperature and pH.

(a)   With reference to **tertiary structure**, explain why enzymes generally only function within a narrow temperature and pH range. (5 marks)

- **Tertiary structure involves interactions between the side chains of amino acids in proteins.**
- **It can include hydrogen-bonding, dipole-dipole forces, dispersion forces, ionic bonding, covalent bonding and/or ion-dipole interactions. (need 4/6)**
- **An increase in temperature can weaken the intermolecular forces including dispersion forces, dipole-dipole forces and/or hydrogen bonding. (need 2/3)**
- **An increase or decrease in pH can impact hydrogen bonding, ionic bonding, ion-dipole interactions. (need 2/3)**
- **These factors can 'denature' or alter the shape of the enzyme rendering it inactive**

One of the principles of green chemistry involves maximising atom economy. Atom economy is a measure of the proportion of reactant atoms that are converted into the desired product in the chemical reaction.

(b)   Calculate the percent atom economy of Step 1.   (2 marks)

% atom economy   =   3 x M(methane) / M(glucose)
=   (3 x 16.042) / 180.156 x 100   (1m)
=   26.71 %   (1m)

High temperature carbonate fuel cells produce 135 kg of hydrogen gas per day using this method. The yield of Step 1 is 94.2% and the yield of Step 2 is 86.8%.

(c)   Calculate the mass of glucose required **each day** to produce this hydrogen. State your answer to the appropriate number of significant figures.   (6 marks)

n(H_2)   =   m/M
=   (135 x 10^3) / 2.016
=   66964.286 mol   (1m)

Step 2 n(H_2)$_{needed}$ =   666964 / 0.868
=   7.71477946 x10^4 mol   (1m)

n(CH_4)   =   1/3 x (7.71477946 x10^4)
=   2.571593153 x10^4 mol   (1m)

Step 3 n(CH_4)   =   (2.571593153 x10^4) / 0.942
=   2.729929038 x10^4 mol   (1m)

n($C_6H_{12}O_6$)   =   1/3 x (2.729929038 x10^4)
=   9.099763459 x10^3 mol   (1m)

m($C_6H_{12}O_6$)   =   (9.099763459 x10^3) x 180.156
=   1639376.986 g
=   1.64 x10^6 g (3 SF)   (1m)

- -

OR

n(H_2)   =   m/M
=   135 x 10^3 / 2.016
=   66964.286 mol   (1m)

n($C_6H_{12}O_6$)   =   1/9 x n(H_2) x (100 / 94.2) x (100 / 86.8)
=   1/9 x 66964.286 x (100 / 94.2) x (100 / 86.8)
=   9099.763 mol   (3m; stoich ratio, yield 1, yield 2)

m($C_6H_{12}O_6$)   =   nM
=   9099.763 x 180.156
=   1639377 g   (1m)

=   1.64 x 10^6 g   OR   1.64 tonnes   (3 SF)   (1m)

(d)   Calculate the volume of air, collected at 15.0 °C and 97.6 kPa, that would be required **each day** to supply sufficient oxygen to react with this hydrogen. Assume air is composed of 21.0% oxygen gas by volume.   (3 marks)

$n(O_2)$ = $1/2 \times n(H_2)$
                 = $1/2 \times 66964.286$
                  =   33482.143 mol   (1m)

$V(O_2)$ = nRT / P
                  = $(33482.143 \times 8.314 \times 288.15) / 97.6$
                  =   821849 L   (1m)

$V(air)$ = $821849 / 0.21$
                  =   3913567 L
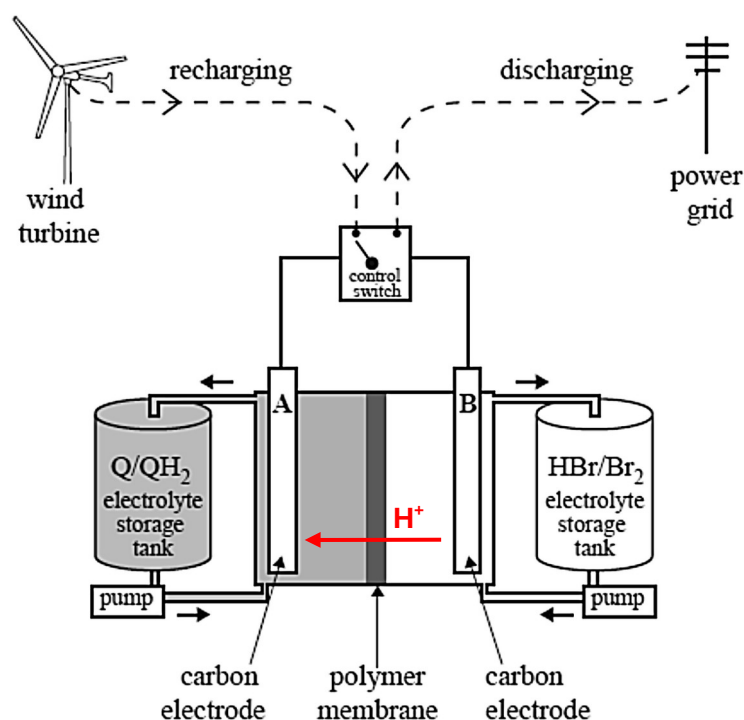   = 3.91×10^6 L   OR   3.91 ML   (3 SF)   (1m)

(e)   Write separate half-equations for the oxidation and reduction processes taking place in Step 1 (assuming acidic conditions).   (2 marks)

Oxidation half-equation	$6H_2O(l) + C_6H_{12}O_6(s) \rightleftharpoons 6CO_2(g) + 24H^+(aq) + 24e^-$
Reduction half-equation	$C_6H_{12}O_6(s) + 24H^+(aq) + 24e^- \rightleftharpoons 6CH_4(g) + 6H_2O(l)$

Question 40 **(8 marks)**

Consider the wind power farm below.

The batteries are recharged using electricity generated by the wind turbines or solar cells. A scientific report, published in January 2014, described a redox flow battery that used a family of chemicals commonly occurring in plants such as rhubarb. These are organic and are known as quinones and hydroquinones. A diagram showing how such a redox flow battery might operate is shown above.

In the diagram, Q represents the quinone and QH_2 represents the corresponding hydroquinone. The researchers made a model of the redox flow battery using aqueous solutions of the redox pairs, Q/QH_2 and Br_2/HBr. Refer to the diagram above. During discharge, QH_2 is converted to Q and Br_2 is converted to HBr.

(a)   Write balanced half-equations for the reactions occurring at the positive and negative electrodes as the cell is discharged.   (2 marks)

Positive electrode: $2e^- + 2H^+ + Br_2 \rightleftharpoons 2HBr$

Negative electrode: $QH_2 \rightleftharpoons Q + 2H^+ + 2e^-$
                                        (if wrong way around, 1 mark)

(b)   Write the overall reaction when the cell is recharged.   (1 mark)

$$2HBr + Q \rightarrow QH_2 + Br_2$$

(c)   The researchers reported that their tests indicated that only hydrogen ions were able to move through the polymer membrane separating the cells.

(i)   Use an arrow ($\rightarrow$ or $\leftarrow$) to indicate the direction of movement of hydrogen ions as the cell is recharged.   **(from B $\rightarrow$ A)**   (1 mark)

(ii)   Why is it important that the other reactants in the half-cells are not able to pass through the polymer?   (2 marks)

-   **To prevent the oxidant and reductant coming into direct contact with each other**

-   **which would cause direct electron exchange rather than through external wire.**

(d)   The researchers also reported that the voltage applied to the cell during recharging was kept below 1.5 V to avoid the electrolysis of water. Write the reduction and oxidation half-equations that occur when water is electrolysed.   (2 marks)

Oxidation: **$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$**

Reduction: **$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$**

                    (if wrong way around, 1 mark)

End of Questions