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CHEMISTRY UNIT 3 & 4 2020

MARKING GUIDE

(25 marks)

(1 mark per

question)

Section One: Multiple-choice

a ■ b □ c □ d □

a ■ b □ c □ d □

a ■ b □ c □ d □

8

9

10

a□b□c□d■ 21 1 11 a □ b □ c ■ d □ a□b□c□d■ 2 12 22 a □ b ■ c □ d □ a□b□c□d■ a □ b □ c ■ d □ 3 23 a□b□c□d■ 13 a ■ b □ c □ d □ a □ b ■ c □ d □ 4 a□b□c■d□ 24 14 a □ b □ c ■ d □ a □ b □ c ■ d □ 5 25 a□b□c■d□ 15 a□b□c□d■ a □ b □ c ■ d □ 6 a □ b □ c ■ d □ 16 $a \square b \blacksquare c \square d \square$ 7 a □ b ■ c □ d □ 17 a ■ b □ c □ d □

a ■ b □ c □ d □

a □ b □ c ■ d □

a□ b■ c□ d□

18

19

20

Section Two: Short answer

35% (76 marks)

This section has **8** 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 (12 marks)

Consider 0.05 mol $L^{\text{-}1}$ 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	K₀ of hydrolysis reaction
NaHCO₃(aq)	$HCO_3^-(aq) + H_2O(I) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$	2.4 x 10 ⁻⁸
KHSO₄(aq)	$HSO_4^-(aq) + H_2O(I) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$	1.2 x 10 ⁻²
Li₃PO₄(aq)	$PO_4^{3-}(aq) + H_2O(I) \rightleftharpoons HPO_4^{2-}(aq) + OH^{-}(aq)$	2.3 x 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	NaHCO₃	Li₃PO₄

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. (6 marks)

In the Li₂CO₃ solution;

 $[H^{+}] = 10^{-pH} = 10^{-10.3}$

 $= 5.01187 \times 10^{-11} \text{ mol L}^{-1}$ (1m)

 $[OH^{-}]$ = $(1.0 \times 10^{-14}) / (5.01187 \times 10^{-11})$

 $= 1.99526 \times 10^{-4} \text{ mol L}^{-1}$ (1m)

Therefore want;

 $c(Ba(OH)_2) = \frac{1}{2} x [OH^-]$

= ½ x 1.99526 x 10⁻⁴ = 9.9763 x 10⁻⁵ mol L⁻¹

9.9763 x 10⁻⁵ mol L⁻¹ (1m)

Using $c_1V_1 = c_2V_2$;

 $V_2 = c_1 V_1 / c_2$

 $= (0.050 \times 0.0085) / 9.9763 \times 10^{-5}$

= 4.2601 L (2m)

 $V_2 - V_1 = 4.2601 - 0.0085$

= 4.252 L needs to be added

= 4.25 L (3 SF) (1m)

OR

In the Li₂CO₃ solution;

 $[H^+] = 10^{-pH}$ $= 10^{-10.3}$

= 5.01187 x 10⁻¹¹ mol L⁻¹

(1m)

[OH⁻] = $(1.0 \times 10^{-14}) / (5.01187 \times 10^{-11})$

= 1.99526 x 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

0.000425 mol (1m)

n(OH⁻) = 2 x n(Ba(OH)₂) = 0.00085 mol

0.00085 mol (1m)

If desired OH concentration is 1.99526 x 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.

Α

В

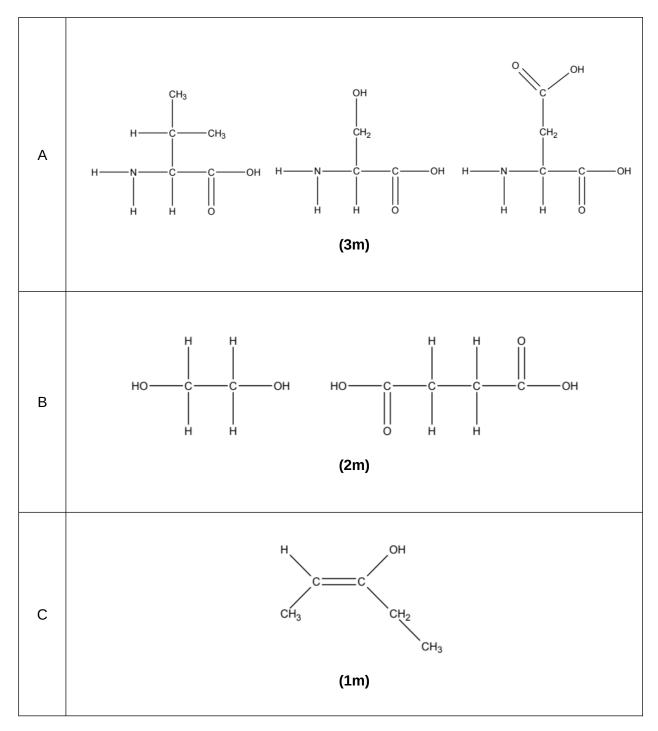
С

(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
С	A B
	_

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

(6 marks)



Question 28 (10 marks)

Consider the two redox reactions below.

Reaction A $Sn^{2+}(aq) + 2 I^{-}(aq) \rightarrow Sn(s) + I_{2}(aq)$

Reaction B $\operatorname{Sn}^{2+}(\operatorname{aq}) + \operatorname{Co}(s) \rightarrow \operatorname{Sn}(s) + \operatorname{Co}^{2+}(\operatorname{aq})$

(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.

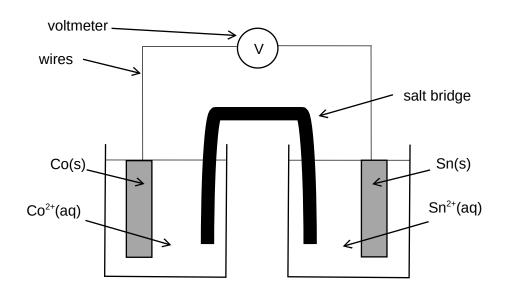
(1m)

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 the equipment and chemicals required to set up the cell. (Note that labels of electrodes, polarity, ion and electron flow are **not** required.) (4 marks)



1m Co/Co²⁺ half-cell 1m Sn/Sn²⁺ half-cell 1m salt bridge 1m wires and voltmeter

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

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)

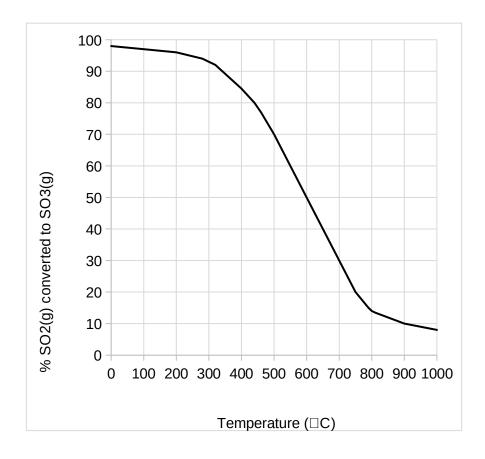
positive electrode	Brown solution forms / colourless solution turns brown
negative electrode	Silver metal plates on electrode / silver solid appears (forms) on electrode

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 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)

	(circle your choice) high OR low (1m)
(i) fastest rate	Justification Increased frequency of collisions, since particles are closer together
	(1m)
	(circle your choice) high OR low (1m)
	Justification
(ii) highest yield	 High pressure favours reaction producing less moles of gas / since gas mole ratio is 3:2
	- The forward reaction would be favoured, increasing yield
	(2m)
	Also accept justification in terms of collision theory, e.g. "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."

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 (9 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.

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

(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 \emph{I} indicates the ratio of ions to molecules in the acid solution is low
- (b) Classify telluric acid as monoprotic or polyprotic (circle your choice). Justify your answer.

monoprotic OR polyprotic (2 marks)

- Two K_a values indicates more than one acidic / ionisable hydrogen / more than one proton donated per molecule
- (c) Label and link the conjugate acid-base pairs in the following equation. (2 marks)

 $H_6TeO_6(aq)$ + $HPO_4^{2-}(aq)$ \rightleftharpoons $H_2PO_4^{-}(aq)$ + $H_5TeO_6^{-}(aq)$ A B CA CB

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.

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

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

Question 31 (8 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 C₅H₁₂O 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 $C_2H_2F_2$ matching each description below. Include **all** bonds and **all** atoms. (2 marks)

The cis geometric isomer	The <i>trans</i> geometric isomer
c==c H	н с — с — н

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

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

Question 32 (13 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 CaCO₃ forms. The reverse process represents the 'dissolution' of solid CaCO₃.

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

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

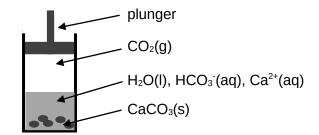
The large quantity of CO₂(g) produced and released into our atmosphere by human activity is having an effect on the carbon equilibria in our oceans.

- (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. (4 marks)
 - An increase in partial pressure of CO₂ increases both reaction rates due to increased frequency of collision (initially only reverse rate is increased, then forward rate increases also)
 - However the reverse reaction rate is increased more than the forward reaction rate
 - This results in a shift to the left / the reverse reaction being favoured
 - More CaCO₃ will dissolve, and therefore the amount of CaCO₃ present is reduced / process of calcification is hindered

- (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 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 CO₂(g) leads to a decrease in ocean pH. (3 marks)

	0	R
Step 1	$CO_2(g) \rightleftharpoons CO_2(aq)$	$CO_2(g) + H_2O(I) \rightleftharpoons H_2CO_3(aq)$
Step 2	$CO_2(aq) + H_2O(I) \rightleftharpoons H_2CO_3(aq)$	$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$
Step 3	$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$	HCO₃ (aq) ⇌ CO₃² (aq) + H⁺(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.



(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 CaCO₃(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, Br₂(aq), is added to each
NaCl(aq)	Orange and colourless solutions mixed, no change observed
Nal(aq)	Orange and colourless solutions mixed, brown solution forms

(b) Write an **ionic equation**, or state 'no reaction', 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
AgNO₃(aq)	2 Ag⁺(aq) + Ni(s) → 2 Ag(s) + Ni²⁺(aq)
ZnSO₄(aq)	No reaction

(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: NaHCO₃(s) / Na₂CO₃(s) / KHCO₃(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.

End of Section Two

Section Three: Extended answer

40% (98 marks)

This section contains **five (5)** 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 34 (20 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;

$$2 \text{ CrO}_4^{2-}(\text{aq}) + 2 \text{ H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{I})$$

yellow 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. (2 marks)

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

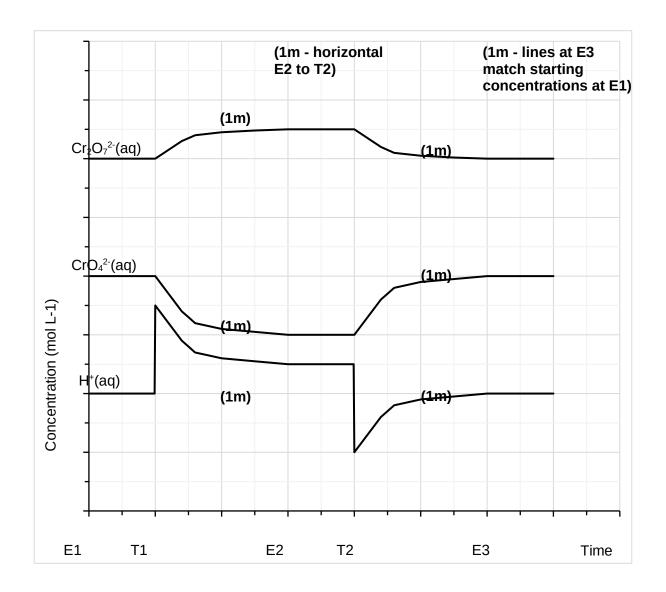
• Firstly, 10 drops of 2 mol L⁻¹ HCl(aq) were added at Time T1, and equilibrium was reestablished at Time E2.

 Next, 10 drops of 2 mol L⁻¹ NaOH(aq) were added at Time T2, and equilibrium was once again re-established at Time E3.

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

The following graph represents the equilibrium in Beaker 1.

$$2 \text{ CrO}_4^{2-}(aq) + 2 \text{ H}^+(aq) \implies \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(1)$$

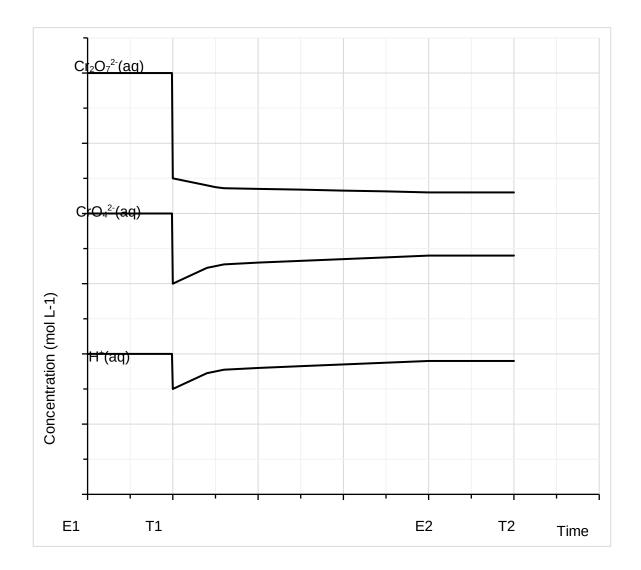


- (b) Plot the concentration for each of the ions shown on the graph, from Time T1 to Time E3. (8 marks)
- (c) Why isn't a curve for water concentration plotted on the graph? (1 mark)
 - Water is the solvent and therefore concentration is not measured / concentration of water assumed to be extremely high and constant (approx. 55 mol L⁻¹)

Beaker 2

The following graph represents the equilibrium in Beaker 2.

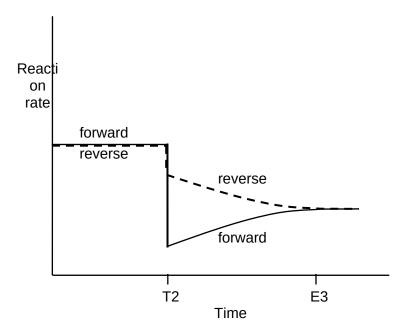
$$2 \text{ CrO}_4^{2-}(aq) + 2 \text{ H}^+(aq) \implies \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(1)$$



- (d) State the change imposed at Time T1. Justify the subsequent equilibrium shift using Le Chatelier's Principle. (3 marks)
 - Addition of (distilled) water
 - Since all aqueous species are diluted, system favours direction which produces greatest number of aqueous species
 - Ratio of aqueous species is 4:1 therefore the reverse reaction is favoured / there is a shift 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 decrease in temperature will favour the exothermic direction
 - Since the system becomes more yellow, the reverse reaction must be favoured
 - 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 35 (16 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	CH ₃	OH H ₂ C O C C C C C C C C C C C C C	CH ₂ C CH ₂ C CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ CH ₂

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
 - Therefore all would undergo addition reactions and decolorise 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. (9 marks)

$$m(C) = 12.01 / 44.01 \times 20.33$$

= 5.5479 g (1m)

$$m(H) = 2.016 / 18.016 \times 4.99$$

= 0.55838 g (1m)

$$m(O) = 7.58 - 5.5479 - 0.55838$$

= 1.4737 g (1m)

	С	Н	0
n	n(c) = m/M	n(H) = m/M	n(O) = m/M
	= 5.5479 / 12.01	= 0.55838 / 1.008	= 1.4737 / 16.00
	= 0.46194 mol	= 0.5539484 mol	= 0.0921073 mol
	(1m)	(1m)	(1m)
ratio	0.46194 / 0.0921073	0.5539484 / 0.0921073	0.0921073 / 0.0921073
(1m)	= 5	= 6	= 1

Therefore EF is C₅H₆O (1m)

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

OR

n(CO ₂) =	m/M 20.33 / 44.01	
=	0.46194 mol	
=	n(c)	(1m)
m(C) =	nM	
=	0.46194 x 12.01	
=	5.5479 g	(1m)
n(H ₂ O) =	4.99 / 18.016	
` =	0.276976 mol	
n(H) =	2 x n(H₂O)	
=	0.5539484 mol	(1m)
m(H) =	nM	
=	0.5539484 x 1.008	
=	0.55838 g	(1m)
m(O) =	7.58 – 5.5479 – 0.55838	
=	1.4737 g	(1m)
n(O) =	m/M	
=	1.4737 / 16.00	
=	0.0921073 mol	(1m)

	С	н	O
n (values from above)	n(c) = 0.46194 mol	n(H) = 0.5539484 mol	n(O) = 0.0921073 mol
ratio (1m)	0.46194 / 0.0921073 = 5	0.5539484 / 0.0921073 = 6	0.0921073 / 0.0921073 = 1

Therefore EF is C₅H₆O (1m)

Substance is 'eugenol' 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 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, Br₂(aq)	chemical test described in part (b)
Organic product formed	OH H ₂ C O C C C C C C C C C C C C C C C C C C	OOH COOH HCCCCCCCCCH2 H CH2 CH2 CH2 CH2 (accept also formation of aldehyde)

 If students incorrectly say 'terpinenol' was identified in part (b), award full marks if their answers in part (c) use terpinenol correctly Question 36 (14 marks)

A beaker contained 135 mL of 0.273 mol L^{-1} hydrochloric acid, HCI(aq). A group of chemistry students were given some 0.198 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) Determine, by calculation, whether all the hydrochloric acid was neutralised upon addition of the ammonia. (4 marks)

n(HCI) = cV

= 0.273 x 0.135 = 0.036855 mol

 $n(NH_3) = cV$

= 0.198 x 0.344 = 0.068112 mol

Since 1:1 stoich ratio, n(NH₃) > n(HCl)

Therefore all the HCl was neutralised (i.e. HCl is the limiting reagent)

(b) Calculate the final concentration, in mol L⁻¹, of any excess reagent present. (2 marks)

 $n(xs NH_3) = 0.068122 - 0.036855$

= 0.031257 mol

 $c(NH_3) = n/V$

= 0.031257 / 0.479 = 0.065255 mol L⁻¹

= 0.0653 mol L⁻¹ (3 SF)

(c) Calculate the final concentration, in mol L⁻¹, of ammonium chloride product. (2 marks)

 $n(NH_4CI) = 0.036855 \text{ mol}$

 $c(NH_4CI) = n/V$

= 0.036855 / 0.479 = 0.0769415 mol L⁻¹ = 0.0769 mol L⁻¹ (3 SF)

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

- (d) 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 NH₃(aq) and NH₄⁺(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_3O^+ and 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 37 (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.

$$\begin{array}{c} O \\ \parallel \\ H_2C-O-C-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \\ \mid O \\ \parallel \\ HC-O-C-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \\ \mid O \\ \parallel \\ H_2C-O-C-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \end{array}$$

- (a) What is biodiesel? Describe how triolein can be converted into biodiesel, by naming the chemical reaction and stating the additional reactant required. (4 marks)
 - Biodiesel is a biofuel with similar uses to diesel
 - It is made from biological material (renewable resources)
 - Made by 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', CH₃(CH₂)₇CH=CH(CH₂)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 =
$$\frac{\text{m(oleic acid)}}{\text{m(oil)}}$$
 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.

```
CH_3(CH_2)_7CH=CH(CH_2)_7COOH + NaOH \rightarrow CH_3(CH_2)_7CH=CH(CH_2)_7COONa + H_2O OR CH_3(CH_2)_7CH=CH(CH_2)_7COOH + OH^- \rightarrow CH_3(CH_2)_7CH=CH(CH_2)_7COO^- + H_2O
```

(1 mark)

(6 marks)

- (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. Then 15.00 mL aliquots of the diluted oil were 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 0.895 g mL⁻¹.

(d) Calculate the % FFA in this batch of waste vegetable oil.

(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

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

 $n(\text{oleic in } 110 \text{ mL}) = 1.25788 \times 10^{-4} / 15 \times 110$

= 9.22445 x 10⁻⁴ mol

= n(oleic in 10 mL sample)

m(oleic) = nM

= 9.22445 x 10⁻⁴ x 282.452

= 0.260547 q

= m / V, therefore

m(oil) = V

= 0.895 x 10 = 8.95 g

% FFAs = $m(oleic) / m(oil) \times 100$

= 0.260547 / 8.95 x 100

= 2.9111 %

= 2.91 % (3 SF)

- (e) State two (2) reasons for performing repeat trials in a titration, in order to obtain an average titre. (2 marks)
 - To minimise random error / so an average can be calculated / to improve accuracy / to improve reliability... (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 3.5 g per litre of vegetable oil, **plus** any extra NaOH that is required to neutralise the FFAs present.

A 2500 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

from part (d)

n(NaOH required to neutralise FFAs in 10 mL oil) = n(oleic in 10 mL) = 9.22445 x 10⁻⁴ mol

n(NaOH required to neutralise 2500 L oil) = 9.22445 x 10⁻⁴ / 0.010 x 2500

= 230.61125 mol

m(NaOH required to neutralise 2500 L oil) = nM

= 230.61125 x 39.998

= 9223.9888 g

m(NaOH required in total for 2500 L) = 8750 + 9223.9888

= 17974 g

= 18 kg (2 SF)

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		
2			
	Differences		
1	 Lipase is a biological catalyst / protein NaOH is an inorganic substance Lipase is temperature / pH sensitive Lipase work by a 'lock and key' mechanism / due to their 		
2	particular shape - Lipase specificity doesn't cause unwanted side reactions (any 2)		

Question 38 (23 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:
$$C_6H_{12}O_6(s) \rightarrow 3CO_2(g) + 3CH_4(g)$$

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:
$$2 H_2(q) + O_2(q) \rightarrow 2 H_2O(1)$$

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)
 - Enzyme function is dependent on correct shape
 - Tertiary structure plays major role in enzyme / protein shape
 - An increase in temperature can weaken the various forces maintaining tertiary structure, eg dispersion, dipole-dipole, H-bonds
 - An increase or decrease in pH can alter the charge of -NH₂ and -COOH groups on amino acids side chains, therefore also affecting tertiary structure
 - These factors '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 = total molar mass of atoms in desired product x 100

total molar mass of atoms in all reactants

% atom economy = $3 \times M(methane) / M(glucose)$

= (3 x 16.042) / 180.156 x 100

= 26.71 %

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)

 $n(H_2) = m/M$

 $= 135 \times 10^3 / 2.016$

= 66964.286 mol (1m)

 $n(C_6H_{12}O_6) = 1/9 \times n(H_2) \times (100 / 94.2) \times (100 / 86.8)$

 $= 1/9 \times 66964.286 \times (100 / 94.2) \times (100 / 86.8)$

= 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 10⁶ 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(O₂) = 1/2 x n(H₂) = 1/2 x 66964.286 = 33482.143 mol

 $V(O_2) = nRT/P$

= (33482.143 x 8.314 x 288.15) / 97.6

= 821849 L

 $V(air) = 821849 \times 100/21$

= 3913567 L

= 3.91 x 10⁶ L OR 3.91 ML (3 SF)

(e) Complete the following table by providing an example of how the 'high temperature carbonate fuel cell' supports the following principles of green chemistry. (3 marks)

Waste prevention	Using landfill to produce energy
Use of renewable feedstocks	Using waste / biological / renewable sugar as starting material
Design less hazardous chemical syntheses	Fuel cells have lower carbon emission / recycling of carbon from biological material into energy

(f) Write separate half-equations for the oxidation and reduction processes taking place in Step 3 (assuming acidic conditions). (2 marks)

Oxidation half-equation	H₂(g) → 2 H⁺(aq) + 2 e ⁻
Reduction half-equation	$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$

- (g) Is a fuel cell classified as a 'galvanic' or 'electrolytic' cell? Justify your answer. (2 marks)
 - Galvanic
 - Reaction produces electrical energy / reaction is spontaneous / reaction has a positive EMF of +1.23 V

End of questions