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# CHEMISTRY

## UNIT 3

### 2020

## MARKING GUIDE

### Section One: Multiple-choice

(25 marks)

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20	a <input type="checkbox"/> b <input type="checkbox"/> c <input checked="" type="checkbox"/> d <input type="checkbox"/>

**Section Two: Short answer****35% (82 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.

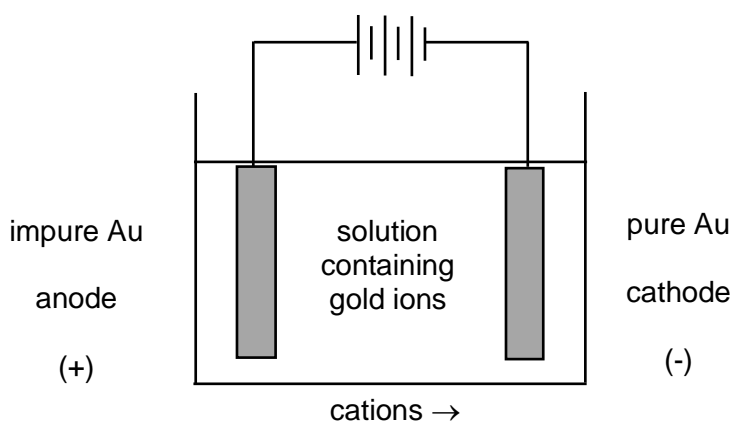
Suggested working time: 60 minutes.

**Question 26****(8 marks)**

The Wohlwill process is used for the electrolytic refining of metallic gold (Au). This method involves a similar process to that of the electrorefining of copper metal.

Sketch a diagram showing how this process could be set up. Your diagram should include the following labels;

- the materials used for the electrodes and electrolyte
- the anode and cathode
- the polarity (sign) of each electrode
- the direction of cation flow



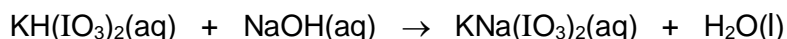
- (1) impure gold electrode label
- (1) pure gold electrode label
- (1) electrolyte containing gold ions label (accept  $\text{Au}^+$  or  $\text{Au}^{3+}$ )
- (1) anode / cathode labels
- (1) polarity (sign) labels
- (1) direction of cation flow label
- (1) power source (label not required)
- (1) other equipment – beaker, wires to electrodes etc (label not required)

**Question 27****(7 marks)**

Potassium hydrogen iodate,  $\text{KH}(\text{IO}_3)_2$ , can be used as a primary standard in acid-base titrations, providing the percentage purity of the solid is known.

An 8.435 g sample of **impure**  $\text{KH}(\text{IO}_3)_2(\text{s})$  was dissolved in distilled water, transferred to a volumetric flask and made up to 500.0 mL. Then 25.00 mL aliquots of this solution were titrated against standardised  $0.05084 \text{ mol L}^{-1} \text{ NaOH}(\text{aq})$ . An average titre of 20.70 mL was required to reach the equivalence point.

The chemical equation for the titration reaction that occurred is given below.



Calculate the percentage purity of the  $\text{KH}(\text{IO}_3)_2(\text{s})$  that was used in this experiment.

$$\begin{aligned} n(\text{NaOH}) &= cV \\ &= 0.05084 \times 0.02070 \\ &= 0.001052388 \text{ mol} \end{aligned} \quad (1)$$

$$n(\text{KH}(\text{IO}_3)_2 \text{ in } 25 \text{ mL}) = 0.001052388 \text{ mol} \quad (1)$$

$$\begin{aligned} n(\text{KH}(\text{IO}_3)_2 \text{ in } 500 \text{ mL}) &= 0.001052388 \times 500 / 25 \\ &= 0.02104776 \text{ mol} \end{aligned} \quad (1)$$

$$= n(\text{KH}(\text{IO}_3)_2 \text{ in powder sample}) \quad (1)$$

$$\begin{aligned} m(\text{KH}(\text{IO}_3)_2) &= nM \\ &= 0.02104776 \times 389.908 \\ &= 8.20669 \text{ g} \end{aligned} \quad \begin{array}{l} (1 \text{ for } M) \\ (1) \end{array}$$

$$\begin{aligned} \% \text{ purity} &= 8.20669 / 8.435 \times 100 \\ &= 97.293 \% \\ &= 97.29\% \quad (4 \text{ SF}) \end{aligned} \quad (1)$$

**Question 28****(12 marks)**

- (a) Write oxidation and reduction half-equations and an overall redox equation for this reaction. You may assume the sulfuric acid is present entirely as  $\text{H}^+(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$ . (6 marks)

Oxidation half-equation  (2)	$\text{Mn}^{2+} + 4 \text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \quad (\text{x2})$ <p style="text-align: center;">OR</p> $\text{Mn}^{2+} + 4 \text{H}_2\text{O} \rightarrow \text{HMnO}_4 + 7 \text{H}^+ + 5 \text{e}^- \quad (\text{x2})$
Reduction half-equation  (2)	$\text{PbO}_2 + 4 \text{H}^+ + \text{SO}_4^{2-} + 2 \text{e}^- \rightarrow \text{PbSO}_4 + 2 \text{H}_2\text{O} \quad (\text{x5})$
Overall redox equation  (2)	$2 \text{Mn}^{2+} + 4 \text{H}^+ + 5 \text{PbO}_2 + 5 \text{SO}_4^{2-} \rightarrow 2 \text{MnO}_4^- + 5 \text{PbSO}_4 + 2 \text{H}_2\text{O}$ <p style="text-align: center;">OR</p> $2 \text{Mn}^{2+} + 6 \text{H}^+ + 5 \text{PbO}_2 + 5 \text{SO}_4^{2-} \rightarrow 2 \text{HMnO}_4 + 5 \text{PbSO}_4 + 2 \text{H}_2\text{O}$

The reaction to produce permanganic acid is performed at a low temperature, to prevent the spontaneous decomposition of  $\text{HMnO}_4(\text{aq})$ .

- (b) Explain, in terms of the collision theory, why a low temperature will inhibit this decomposition reaction. (4 marks)

**A low temperature will cause a**

**(1) decrease in average kinetic energy**

**(1) decrease in proportion of successful collisions**

**(1) decrease in frequency of collision**

**(1) therefore reaction rate (i.e. the decomposition) is decreased / inhibited**

Permanganic acid is known to be a strong acid.

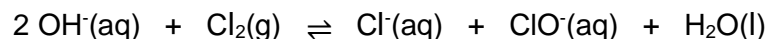
- (c) Write the  $K_a$  expression for permanganic acid and give an indication of the expected  $K_a$  value. (2 marks)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{MnO}_4^-]}{[\text{HMnO}_4]} \quad (1)$$

**(1) value expected to be high / greater than 1**

**Question 29****(10 marks)**

Consider the following reaction that has been allowed to establish equilibrium.



The following table considers the effects of imposing different changes upon this system.

- (a) Complete the following table by predicting which direction would be favoured, as well as the resulting effect on the concentration of  $\text{ClO}^-(\text{aq})$  when compared with the original equilibrium. Consider each of the imposed changes in isolation. (8 marks)

<b>Imposed change</b>	<b>Favoured direction</b> (forward, reverse, no shift)	<b>Effect on final concentration of <math>\text{ClO}^-(\text{aq})</math></b> (increase, decrease, no change)
A small amount of $\text{NaClO}(\text{s})$ was added	<b>reverse</b>	<b>increase</b>
The volume of the canister was decreased	<b>forward</b>	<b>increase</b>
Distilled water was added	<b>no shift</b>	<b>decrease</b>
Several drops of $2 \text{ mol L}^{-1} \text{Mg}(\text{NO}_3)_2(\text{aq})$ was added	<b>reverse</b>	<b>decrease</b>

A chemist decided to verify their predictions experimentally. They set up the equilibrium system described above, created the various imposed changes described in part (a) and examined the results.

- (b) Would the equilibrium system in this experiment be considered 'open' or 'closed' when the imposed changes were being made? Justify your answer. (2 marks)

**(1) open**

**(1) adding substances into system implies matter is being exchanged**

**Question 30****(10 marks)**

A water tank contained 25.0 kL of contaminated water with a pH of 10.1. A chemist decided to add some solid acetylsalicylic acid crystals to the water tank, to lower the pH. Acetylsalicylic acid is a monoprotic acid with the formula  $\text{C}_9\text{H}_8\text{O}_4$  ( $M = 180.158 \text{ g mol}^{-1}$ ).

Calculate the mass of acetylsalicylic acid crystals that should be added to the tank and dissolved in the water, to lower the pH to 7.8.

**At pH 10.1;**

$$[\text{H}^+] = 10^{-10.1} = 7.94328 \times 10^{-11} \text{ mol L}^{-1} \quad (1)$$

$$[\text{OH}^-] = 10^{-14} / 10^{-10.1} = 1.258925 \times 10^{-4} \text{ mol L}^{-1} \quad (1)$$

$$\begin{aligned} n(\text{OH}^-) &= cV \\ &= 1.258925 \times 10^{-4} \times 25\,000 \\ &= 3.1473125 \text{ mol} \end{aligned} \quad (1)$$

**At pH 7.8;**

$$[\text{H}^+] = 10^{-7.8} = 1.584893 \times 10^{-8} \text{ mol L}^{-1} \quad (1)$$

$$[\text{OH}^-] = 10^{-14} / 10^{-7.8} = 6.309573 \times 10^{-7} \text{ mol L}^{-1} \quad (1)$$

$$\begin{aligned} n(\text{OH}^-) &= cV \\ &= 6.309573 \times 10^{-7} \times 25\,000 \\ &= 0.015773933 \text{ mol} \end{aligned} \quad (1)$$

$$\begin{aligned} n(\text{OH}^- \text{ at pH } 10.1) - n(\text{OH}^- \text{ at pH } 7.8) &= 3.1473125 - 0.015773933 \\ &= 3.1315386 \text{ mol} \end{aligned} \quad (1)$$

Therefore want to add 3.1315386 mol of  $\text{H}^+$  (1)

Since monoprotic, need  $n(\text{C}_9\text{H}_8\text{O}_4) = 3.1315386 \text{ mol}$  (1)

$$\begin{aligned} m(\text{C}_9\text{H}_8\text{O}_4) &= nM \\ &= 3.1315386 \times 180.158 \\ &= 564.17 \text{ g} \\ &= 564 \text{ g} \end{aligned} \quad (1)$$

**Question 31****(11 marks)**

A chemistry class was given four (4) jars labelled A, B, C and D.

- (a) Identify metals A and D. (2 marks)

A	<b>Nickel</b>
D	<b>Cobalt</b>

To distinguish between metals B and C, one student suggested adding a piece of each to separate solutions of aqueous nickel bromide,  $\text{NiBr}_2(\text{aq})$ .

- (b) Justify how this would allow metals B and C to be distinguished. Include observations for both samples and a relevant chemical equation in your answer. (5 marks)

**(1) tin metal would not react with the  $\text{NiBr}_2(\text{aq})$  where as cadmium metal would react with  $\text{NiBr}_2(\text{aq})$**

**(1) reaction with cadmium has  $\text{EMF} > 0$  / reaction is spontaneous OR reaction with tin has  $\text{EMF} < 0$  / is non-spontaneous**

**(1) observations with tin metal – solution would remain green**

**(1) observations with cadmium metal – green solution would fade as silver metal dissolves, new silver / grey metal / precipitate produced**

**(1)  $\text{Cd}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Ni}(\text{s}) + \text{Cd}^{2+}(\text{aq})$**

- (c) Using the results of this investigation, how would the students be able to identify which of the metals (A, B, C or D) was the strongest reducing agent (reductant)? (2 marks)

**(1) whichever metal of B or C that reacted with  $\text{NiBr}_2(\text{aq})$  would be the strongest reductant**

**(1) this is because it would be the metal most easily oxidised / the metal with the highest oxidation potential**

Another test tube containing  $\text{NiBr}_2(\text{aq})$  was set up and some chlorine water was added to this solution. The test tube was stoppered and gently shaken.

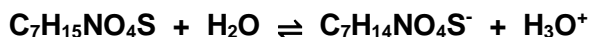
- (d) Write oxidation and reduction half-equations for the reaction that would occur. (2 marks)

Oxidation half-equation	<b><math>2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-</math></b>
Reduction half-equation	<b><math>\text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^-</math></b>

**Question 32****(12 marks)**

The molecular formula of MOPS is  $C_7H_{15}NO_4S$ . MOPS is a weak, monoprotic acid.

- (a) Write a Bronsted-Lowry equation illustrating how MOPS dissolves in water. Use the molecular formula given. (2 marks)



(1) reactants and products

(1) double arrows

- (b) Give the molecular formula of the sodium salt of MOPS. (1 mark)

(1)  $NaC_7H_{14}NO_4S$  /  $C_7H_{14}NO_4SNa$

A solution was made by dissolving 75 g of the sodium salt of MOPS into 200 mL of distilled water.

- (c) Justify, with the use of a relevant chemical equation, whether the pH of this solution would be acidic, basic or neutral. (3 marks)

(1) basic

(1) anion of a weak acid will hydrolyse with water to produce  $OH^-$  ions

(1)  $C_7H_{14}NO_4S^- + H_2O \rightleftharpoons C_7H_{15}NO_4S + OH^-$

An **equal mass** of solid MOPS was then added to the beaker containing the solution of the sodium salt. The mixture was stirred until all solid had dissolved.

A student tested the buffering capacity of the resulting solution. They were able to add 9 mL of  $1 \text{ mol L}^{-1}$   $NaOH(aq)$  before the pH of the buffer rose significantly. However, they were only able to add 6 mL of  $1 \text{ mol L}^{-1}$   $HCl(aq)$  before a similar fall in pH was noted.

- (d) Define 'buffering capacity'. (2 marks)

(1) The extent to which a buffer solution can maintain its pH

(1) upon addition of excess strong acid or base /  $H_3O^+$  or  $OH^-$

- (e) Explain why this buffer solution had a higher buffering capacity upon addition of excess base. (4 marks)

The same mass of conjugate acid-base pair was dissolved;

(1) since the M of the conjugate base ( $NaC_7H_{14}NO_4S$ ) is higher

OR since the M of the conjugate acid ( $C_7H_{15}NO_4S$ ) is lower

(1) this equates to fewer moles / lower concentration of conjugate base ( $C_7H_{14}NO_4S^-$ ) present

OR this equates to greater moles / higher concentration of conjugate acid

( $C_7H_{15}NO_4S$ ) present

(1) therefore there is less base available to react with added acid /  $H_3O^+$

OR therefore there is more acid available to react with added base /  $OH^-$

(1) so the buffer has a greater ability to maintain pH / higher buffering capacity upon addition of base /  $OH^-$



**Question 33****(12 marks)**

- (a) State the values that would be used when setting up the hydrogen half-cell under standard conditions. (2 marks)

Partial pressure of $\text{H}_2(\text{g})$	<b>100 kPa</b>
Concentration of $\text{H}^+(\text{aq})$	<b>1 mol L<sup>-1</sup></b>

A standard hydrogen half-cell was joined by wires and a salt bridge to a second half-cell. Two different experiments were performed;

- In Experiment 1, the  $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$  half-cell was used.
- In Experiment 2, the  $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$  half-cell was used.

- (b) In which experiment would the greater EMF have been produced? State the value of this EMF. (2 marks)

**(1) Experiment 1 / silver half-cell**

**(1) EMF = +0.80 V**

- (c) Discuss how the role of the hydrogen half-cell differs in Experiment 1 and 2. Include a relevant half-equation for the hydrogen half-cell in each case. (6 marks)

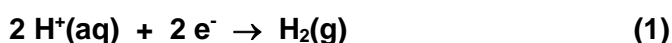
**In Experiment 1 the hydrogen half-cell (2) for any 2 of the following**

- **is the anode**
- **is the site where oxidation occurs**
- **has a negative (-) polarity**
- **has a lower reduction potential than  $\text{Ag}/\text{Ag}^+$**



**In Experiment 2 the hydrogen half-cell (2) for any 2 of the following**

- **is the cathode**
- **is the site where reduction occurs**
- **has a positive (+) polarity**
- **has a higher reduction potential than  $\text{Zn}/\text{Zn}^{2+}$**



- (d) State the function of the salt bridge in this experiment. (2 marks)

**(1) to complete the circuit / allow the flow of electricity**

**(1) maintain electrical neutrality of half-cells / allow ion migration between half-cells**

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.

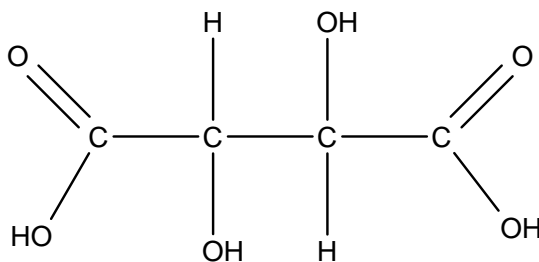
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**Question 34****(24 marks)**

The pH of wine is usually between 2.9 - 3.9, depending on the type of wine and the type of grapes used to make the wine. The 'total acidity' of wine, is a measure of the total amount of all the various acids present in wine. This is also referred to as the '**total ionisable hydrogen**' present, i.e. all the hydrogen in the wine that has the ability to ionise and contribute to overall acidity.

The total acidity of wine is monitored carefully during the winemaking process. Too much acid can result in the wine being sour, whilst too little can cause the wine to taste flat and lack freshness. Total acidity is measured before the grapes are harvested, after the wine is produced, and then as the wine ages. There are many different weak acids that are found in wine, such as tartaric acid, malic acid, citric acid and succinic acid.

Generally, the most abundant acid found in wine is tartaric acid,  $C_4H_6O_6$ . Tartaric acid is a weak, diprotic acid found in grapes, as well as other fruits such as bananas, tamarinds and citrus fruits. Its chemical structure is shown below.



Grapes that are grown in a warmer climate usually contain lower concentrations of tartaric acid than those grown in cooler climates. The concentration of tartaric acid from grapes grown in warmer regions is generally in the range of  $2-3 \text{ g L}^{-1}$ , whilst for grapes grown in cooler areas the concentration is around  $6 \text{ g L}^{-1}$ .

To determine the total acidity of wine, a titration is performed. A sample of wine is titrated against a strong base, and the number of moles of  $\text{OH}^-(\text{aq})$  required to reach the equivalence point is said to be equal to the number of moles of '**total ionisable hydrogen**' present in the wine.

A  $10.00 \text{ mL}$  sample of wine was taken and made up to  $100.0 \text{ mL}$  with distilled water. Then  $20.00 \text{ mL}$  aliquots of the dilute wine were titrated against a standard solution of  $0.01575 \text{ mol L}^{-1} \text{ KOH}(\text{aq})$ . An average titre of  $16.73 \text{ mL}$  was required to reach equivalence.

- (a) Calculate the concentration of 'total ionisable hydrogen' in the 10.00 mL sample of wine. State your answer to the appropriate number of significant figures. (6 marks)

$$\begin{aligned} n(\text{KOH}) &= cV \\ &= 0.01575 \times 0.01673 \\ &= 0.000263498 \text{ mol} \end{aligned} \quad (1)$$

$$n(\text{total ionisable hydrogen in 20 mL}) = 0.000263498 \text{ mol} \quad (1)$$

$$\begin{aligned} n(\text{total ionisable hydrogen in 100 mL}) &= 0.000263498 \times (100 / 20) \\ &= 0.0013175 \text{ mol} \end{aligned} \quad (1)$$

$$= n(\text{total ionisable hydrogen in wine}) \quad (1)$$

$$\begin{aligned} c(\text{total ionisable hydrogen}) &= n / V \\ &= 0.0013175 / 0.01 \\ &= 0.131749 \text{ mol L}^{-1} \end{aligned} \quad (1)$$

$$= 0.1317 \text{ mol L}^{-1} \quad (4 \text{ SF}) \quad (1)$$

Using a digital pH meter, the pH of the wine was measured to be 3.2.

- (b) Calculate the concentration of hydronium (hydrogen) ions present in the wine. Justify why this concentration does not match the concentration of 'total ionisable hydrogen' calculated in part (a). (3 marks)

$$\begin{aligned} [\text{H}^+] &= 10^{-3.2} \\ &= 0.0006309 \text{ mol L}^{-1} \end{aligned} \quad (1)$$

The acids in wine are weak and therefore only partially ionised (1)

In a titration, all ionisable hydrogen reacts and is neutralised – the 'total ionisable hydrogen' is always therefore much greater than the concentration of hydrogen ions present in wine (1)

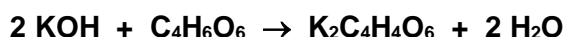
Since tartaric acid is **diprotic**, there are two possible salts that can be produced in a neutralisation reaction with potassium hydroxide solution; potassium bitartrate ( $\text{KC}_4\text{H}_5\text{O}_6$ ) and potassium tartrate ( $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ ). One of these salts is acidic and one is basic.

- (c) Complete the table below, by classifying each salt as acidic or basic. Give a relevant hydrolysis equation to support each of your choices. (3 marks)

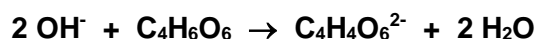
Salt	Acidic / Basic	Equation
$\text{KC}_4\text{H}_5\text{O}_6$	<b>acidic</b> (1)	$\text{C}_4\text{H}_5\text{O}_6^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_4\text{H}_4\text{O}_6^{2-} + \text{H}_3\text{O}^+ \quad (1)$
$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$	<b>basic</b>	$\text{C}_4\text{H}_4\text{O}_6^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{C}_4\text{H}_5\text{O}_6^- + \text{OH}^- \quad (1)$

The pH at the equivalence point of this titration is known to be approximately 8.2.

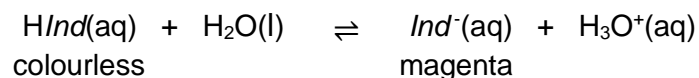
- (d) Use this information to write a balanced equation for the reaction that takes place between potassium hydroxide and tartaric acid in this titration. (2 marks)



OR



The acid-base indicator phenolphthalein is used in this titration. The general equation below can be used to represent phenolphthalein indicator.



- (e) State the colour change that would be observed in the conical flask during this titration. Justify how this colour change occurs, using the equation above and Le Chatelier's principle. (5 marks)

**(1) colourless to magenta**

**(1) initially only acidic wine is present, therefore an excess of  $\text{H}_3\text{O}^+(\text{aq})$**

**(1) thus the reverse reaction is favoured and indicator appears colourless**

**(1) as  $\text{KOH(aq)}$  is added this neutralises the  $\text{H}_3\text{O}^+(\text{aq})$**

**(1) the forward reaction is thus favoured resulting in the magenta colour**

It is known that 62.4% of the 'total ionisable hydrogen' in this particular wine was contributed by tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ).

- (f) Calculate the concentration of tartaric acid in the wine in grams per litre ( $\text{g L}^{-1}$ ). State (by circling your choice below) whether the grapes used to make this wine are likely to have been grown in a warm or cool climate. (5 marks)

**From part (a),  $c(\text{total ionisable hydrogen}) = 0.1317 \text{ mol L}^{-1}$**

**$c(\text{H}^+ \text{ from tartaric}) = 62.4 / 100 \times 0.131749$   
 $= 0.08221122 \text{ mol L}^{-1}$  (1)**

**$c(\text{tartaric}) = \frac{1}{2} \times c(\text{H}^+)$   
 $= 0.0411056 \text{ mol L}^{-1}$  (1)**

**$m(\text{tartaric in 1 L}) = nM$   
 $= 0.0411056 \times 150.088$   
 $= 6.16946 \text{ g}$  (1)**

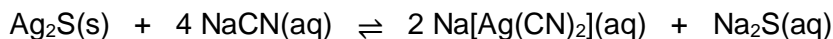
**Therefore concentration of tartaric acid in wine is  $6.17 \text{ g L}^{-1}$  (1)**

Grapes were most likely grown in a; warm climate / cool climate (1)

(no mark for circling 'cool climate' in the absence of any working out)

**Question 35****(19 marks)**

Silver metal can be extracted from the ore 'argentite' which contains the compound  $\text{Ag}_2\text{S}(\text{s})$ . In the first step of this extraction process, the ore containing  $\text{Ag}_2\text{S}(\text{s})$  is crushed, and then a solution of sodium cyanide,  $\text{NaCN}(\text{aq})$ , is added to leach the silver out of the ore. This forms the complex ion sodium argentocyanide,  $\text{Na}[\text{Ag}(\text{CN})_2](\text{aq})$ , as shown in the equation below.



- (a) Write the equilibrium constant expression for this reaction.

**(2 marks)**

$$K = \frac{[\text{Na}[\text{Ag}(\text{CN})_2]]^2 [\text{Na}_2\text{S}]}{[\text{NaCN}]^4}$$

**(2) if completely correct**  
**(1) may be allocated for minor error, such as missing 'K='**  
**or one index or subscript incorrect**

If 12.5 kL of  $5.0 \text{ g L}^{-1}$   $\text{NaCN}(\text{aq})$  was added to the leaching tank and poured over the crushed ore;

- (b) Calculate the maximum mass of  $\text{Ag}_2\text{S}(\text{s})$  that could react.

**(4 marks)**

$$\begin{aligned} m(\text{NaCN}) &= cV \\ &= 5 \times 12500 \\ &= 62500 \text{ g} \end{aligned} \quad (1)$$

$$\begin{aligned} n(\text{NaCN}) &= m / M \\ &= 62500 / 49.01 \\ &= 1275.25 \text{ mol} \end{aligned} \quad (1)$$

$$\begin{aligned} n(\text{Ag}_2\text{S}) &= \frac{1}{4} \times n(\text{NaCN}) \\ &= \frac{1}{4} \times 1275.25 \\ &= 318.812 \text{ mol} \end{aligned} \quad (1)$$

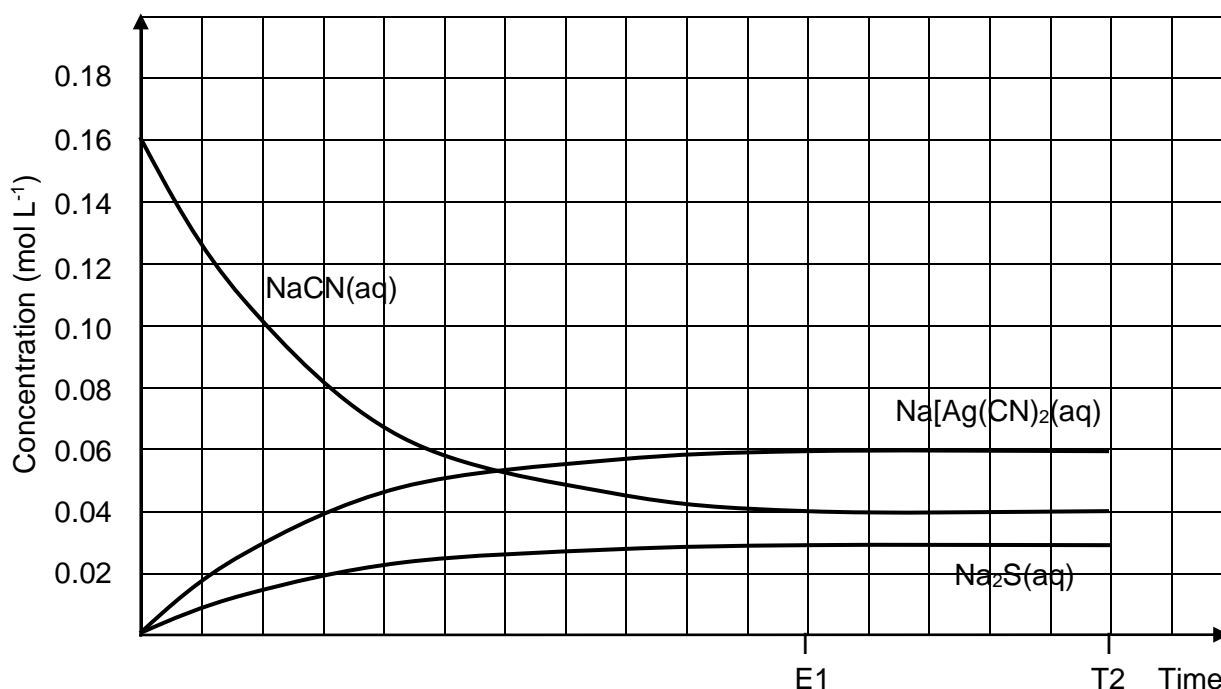
$$\begin{aligned} m(\text{Ag}_2\text{S}) &= nM \\ &= 318.812 \times 247.87 \\ &= 79024.05 \text{ g} \\ &= 79 \text{ kg} \end{aligned} \quad (1)$$

- (c) Explain, in terms of the collision theory, why the ore is crushed before mixing with the  $\text{NaCN(aq)}$  solution. (3 marks)

**(1) Crushing the ore increases surface area / state of subdivision of  $\text{Ag}_2\text{S(s)}$**   
**(1) This will increase the frequency of collision between reactants**  
**(1) Therefore a faster reaction rate occurs**

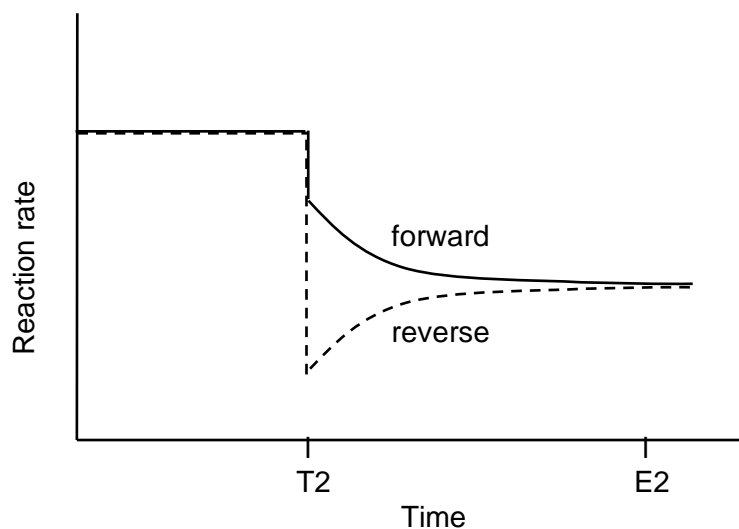
A particular leach tank contained an excess mass of crushed argentite ore containing  $\text{Ag}_2\text{S(s)}$ . A  $0.16 \text{ mol L}^{-1}$  solution of  $\text{NaCN(aq)}$  was poured over the ore, and the reactants were mixed. At Time E1, equilibrium was established. The concentration of the  $\text{NaCN(aq)}$  was measured again and found to be  $0.04 \text{ mol L}^{-1}$ .

- (d) On the axes below, sketch curves showing the concentration of all relevant species, from Time 0 until the establishment of equilibrium at Time E1. Continue your curves from Time E1 to Time T2. Label each curve. (5 marks)



- (1) NaCN line correctly drawn**  
**(1)  $\text{Na[Ag(CN)}_2\text{]}$  line correctly drawn**  
**(1)  $\text{Na}_2\text{S}$  line correctly drawn**  
**(1) Labels on each line**  
**(1) Horizontal lines E1 to T2**

At Time T2, a temperature change is imposed on the system. The following rate graph was drawn to illustrate the effects of this imposed change.



- (e) State whether the temperature was increased or decreased at Time T2. (1 mark)

**(1) decreased**

- (f) Justify, using the information provided in the rate graph above, whether the forward reaction is endothermic or exothermic. (4 marks)

**(1) the forward reaction rate is not decreased as much as the reverse reaction rate**  
**(1) this shows that the forward reaction has been favoured**  
**(1) a temperature decrease will favour the exothermic direction (in order to produce more heat)**  
**(1) therefore the forward reaction must be exothermic**



**Question 36****(19 marks)**

- (a) Write oxidation and reduction half-equations and an overall equation to represent the reaction occurring in the PEM fuel cell. Calculate the EMF produced under standard conditions. (4 marks)

Reduction half-equation	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$
Oxidation half-equation	$\text{H}_2(\text{g}) \rightarrow 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$
Overall equation	$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$
EMF under standard conditions	$+1.23 \text{ V}$

- (b) At which electrode are protons produced? Justify your answer. (2 marks)

**(1) produced at the anode**  
**(1) protons are hydrogen ions /  $\text{H}^+$**

- (c) Why must the PEM have the ability to conduct protons but **not** electrons? (2 marks)

**(1) must conduct protons to act as the salt bridge / allow internal flow of charge / maintain electrical neutrality**  
**(1) must NOT conduct electrons as cell would short circuit / an unwanted direct reaction may occur**

- (d) Justify why fuel cells and lithium-ion batteries can both be classified as 'galvanic' cells. (2 marks)

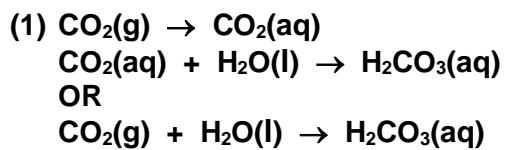
**(1) both produce electrical energy from chemical energy**  
**(1) both involve a spontaneous redox reaction / have a positive EMF**

- (e) Classify the lithium-ion battery as a 'primary' or 'secondary' cell. Justify your choice using the information provided. (3 marks)

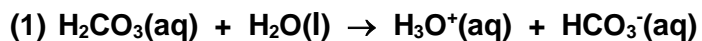
**(1) secondary**  
**(1) diagram states that lithium-ion cells store energy produced by fuel cells**  
**(1) this means they must be able to be charged and discharged**

- (f) Describe, using relevant chemical equations, how an increase in atmospheric  $\text{CO}_2(\text{g})$  has led to a decrease in the pH of our oceans. (6 marks)

**(1) Atmospheric carbon dioxide dissolves in water to produce carbonic acid**



**(1) The carbonic acid ionises to produce hydronium ions**



**(1) Since  $\text{pH} = -\log[\text{H}_3\text{O}^+]$  / since this results in an increased concentration of  $\text{H}_3\text{O}^+(\text{aq})$**

**(1) This leads to a decrease in pH**

**Question 37****(18 marks)**

A group of chemistry students were comparing and contrasting two different acid-base titrations. They set up 'Titration A' and 'Titration B' as follows;

	<b>Titration A</b>	<b>Titration B</b>
Substance in conical flask	20.00 mL of 0.10 mol L <sup>-1</sup> NaOH(aq)	20.00 mL of 0.10 mol L <sup>-1</sup> NaOH(aq)
Substance in burette	0.10 mol L <sup>-1</sup> HCl(aq)	0.10 mol L <sup>-1</sup> CH <sub>3</sub> COOH(aq)
Sketch of titration curve		

- (a) In the table above, label the equivalence point on **both** titration curves. (2 marks)

**(1) For each graph, see arrows (should be located midpoint of vertical drop)**

- (b) State the pH at the equivalence point in Titration A. Justify your answer. (3 marks)

**(1) 7**

**(1) The salt produced (NaCl) is neutral and does not hydrolyse**

**(1) Therefore the concentration of H<sub>3</sub>O<sup>+</sup>(aq) is equal to the concentration of OH<sup>-</sup>(aq)**

- (c) In Titration A, state the volume of HCl(aq) that would have been added from the burette to reach the equivalence point. (Note that a calculation is not required.) (1 mark)

**(1) 20 mL**

- (d) Would the volume of  $\text{CH}_3\text{COOH}(\text{aq})$  required to reach the equivalence point in Titration B be higher, lower or equal to the volume of  $\text{HCl}(\text{aq})$  required in Titration A? Circle your choice below, and briefly justify your answer. (2 marks)

higher

lower

equal

(1)

**(1) Equal volumes and concentrations used and both acids are monoprotic  
(therefore will require the same moles of base to neutralise)**

The students decided to investigate Titration A in more detail. Once they had successfully reached the equivalence point, they added 5 extra drops of  $\text{HCl}(\text{aq})$ .

- (e) Calculate the pH of the resulting solution within the conical flask. Assume the volume of 1 drop is equal to 0.05 mL. (5 marks)

$$\begin{aligned} V(\text{HCl}) &= 5 \times 0.05 \times 10^{-3} \\ &= 0.00025 \text{ L} \end{aligned} \quad (1)$$

$$\begin{aligned} n(\text{HCl}) &= cV \\ &= 0.1 \times 0.00025 \\ &= 2.5 \times 10^{-5} \text{ mol} \\ &= n(\text{H}^+) \end{aligned} \quad (1)$$

$$\begin{aligned} c(\text{H}^+) &= n / V \\ &= 2.5 \times 10^{-5} / 0.04025 \end{aligned} \quad (1 \text{ for } V)$$

$$= 6.211 \times 10^{-4} \text{ mol L}^{-1} \quad (1)$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (6.211 \times 10^{-4}) \\ &= 3.207 \\ &= 3.2 \end{aligned} \quad (1)$$

As can be seen in the curve for Titration B, if extra  $\text{CH}_3\text{COOH}(\text{aq})$  is added after the equivalence point has been reached, the change in pH is much less pronounced. In fact, the addition of 5 extra drops of  $\text{CH}_3\text{COOH}(\text{aq})$  lowers the pH by much less than 2 units.

- (f) Complete the table below, by listing the next two **compounds** with highest concentration (after water) that would be present in the conical flask for Titration B, when 5 drops of  $\text{CH}_3\text{COOH}(\text{aq})$  has been added past the equivalence point. (2 marks)

Titration A	Titration B
1. $\text{H}_2\text{O}(\text{l})$	1. $\text{H}_2\text{O}(\text{l})$
2. $\text{NaCl}(\text{aq})$	2. <b><math>\text{NaCH}_3\text{COO}(\text{aq})</math></b>
3. $\text{HCl}(\text{aq})$	3. <b><math>\text{CH}_3\text{COOH}(\text{aq})</math></b>

Further addition of  $\text{CH}_3\text{COOH}(\text{aq})$  past the equivalence point (the region indicated by \* on the titration curve) continues to cause a much smaller change in pH, compared to Titration A.

- (g) Justify why, upon addition of excess acid after equivalence, the change in pH in Titration B occurs to a much lesser degree than in Titration A. (3 marks)

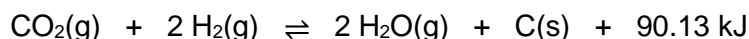
**(1) A buffer solution is formed**

**(1) Due to the presence of the weak conjugate acid-base pair  $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$**

**(1) Therefore the pH change upon addition of excess acid is not as great as in Titration A where no buffer solution is formed**

**Question 38****(18 marks)**

The equation for the Bosch reaction is given below.



- (a) State the change imposed on the system at Time T1. (1 mark)

**(1) Volume decreased / halved**

- (b) Explain, in terms of the collision theory, the effect of the imposed change at Time T1 on the position of equilibrium. (4 marks)

**(1) Both forward and reverse reaction rates are increased**

**(1) Same amount of gas particles are in a smaller space, therefore frequency of collision is increased**

**(1) Since the ratio of gas particles is 3:2, the forward reaction rate is increased more than the reverse reaction rate**

**(1) This results in a shift to the right / the products being favoured**

- (c) State the change imposed on the system at Time T2, as well as the effect this change has on the position of equilibrium. (2 marks)

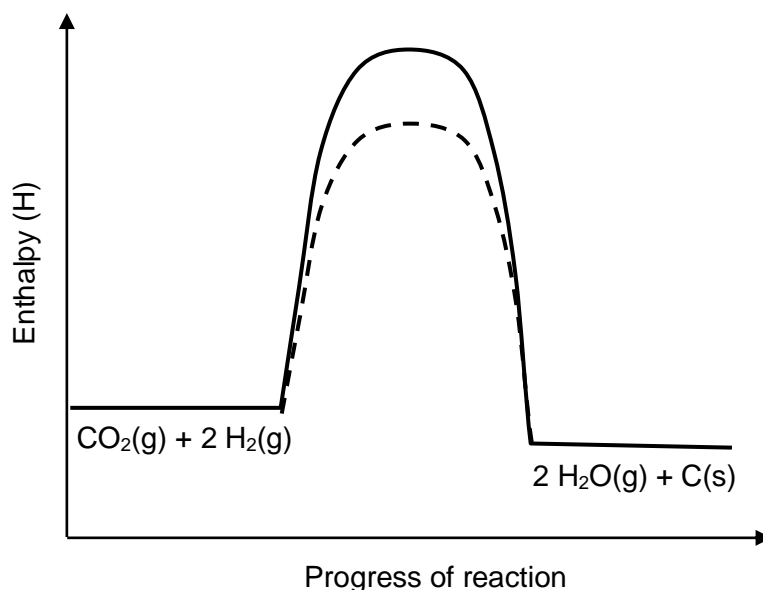
**(1) Water vapour removed**

**(1) Equilibrium will shift right / favour forward reaction**

- (d) Complete the table below, regarding the changes that would be observed in reaction rate in response to the change imposed at Time T2. In each box of the table, write either 'increased', 'decreased' or 'no change'. Your answers should be stated in comparison to the previous equilibrium that had been established at Time E2. (4 marks)

	<b>Immediate change in rate</b> (increase / decrease / no change)	<b>Final / overall change in rate</b> (increase / decrease / no change)
Forward reaction	<b>none</b>	<b>decrease</b>
Reverse reaction	<b>decrease</b>	<b>decrease</b>

The energy profile diagram for the Bosch reaction is shown below. The reaction has a very high activation energy and must be carried out at a temperature greater than 450 °C. It is only mildly exothermic.



- (e) Comment on the likely reversibility of this reaction. (2 marks)

**(1) Not likely to be reversible / reverse reaction is less likely to occur than forward reaction**

**(1) Activation energy is high in the forward direction and high temperatures are required, therefore reverse reaction is unlikely to occur as reverse activation energy is even higher**

**(Marks may be awarded if students argue that the reverse reaction would potentially also occur, under conditions of high temperature, since the activation energy for the reverse is only slightly higher than forward)**

- (f) Add to the energy profile diagram above, by indicating the effect of including metallic iron in the reaction system. (1 mark)

**(1) See dashed line on energy profile diagram above**

- (g) Explain, in terms of the collision theory, the role of the iron in this reaction. (4 marks)

**(1) Provides an alternate reaction pathway**

**(1) With a lower activation energy**

**(1) Therefore a greater proportion of particles can react / have collision energy greater than activation energy**

**(1) Reaction rate is increased**

**(1m may be awarded for discussion of how orientation of collision can be improved by adsorption/desorption of reactants onto catalyst etc)**

End of questions