

Chemistry-Semester 1 2016-Unit 3-Marking Key

Section One: Multiple-choice

(50 marks)

1. a	2. c	3. c	4. b	5. c
6. a	7. a	8. c	9. c	10. a
11. b	12. d	13. b	14. b	15. b
16. b	17. d	18. a	19. b	20. c
21. d	22. b	23. c	24. d	25. c

Section Two: Short answer

(70 marks)

Question 26

(6 marks)

Arsenic acid (H_3AsO_4) can be produced by reacting solid arsenic trioxide (As_2O_3) with nitric acid. This produces arsenic acid, as well as the gaseous by-product dinitrogen trioxide.

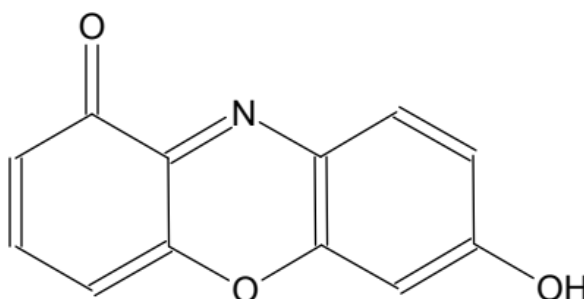
Write the oxidation and reduction half-equations and the overall redox equation for this reaction, assuming acidic conditions.

Oxidation half-equation	$\text{As}_2\text{O}_3 + 5 \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{AsO}_4 + 4 \text{H}^+ + 4 \text{e}^- \quad (2)$
Reduction half-equation	$2 \text{NO}_3^- + 6 \text{H}^+ + 4 \text{e}^- \rightarrow \text{N}_2\text{O}_3 + 3 \text{H}_2\text{O} \quad (2)$ OR $2 \text{HNO}_3 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow \text{N}_2\text{O}_3 + 3 \text{H}_2\text{O} \quad (1)$
Overall redox equation	$\text{As}_2\text{O}_3 + 2 \text{H}_2\text{O} + 2 \text{NO}_3^- + 2 \text{H}^+ \rightarrow 2 \text{H}_3\text{AsO}_4 + \text{N}_2\text{O}_3 \quad (2)$ OR $\text{As}_2\text{O}_3 + 2 \text{H}_2\text{O} + 2 \text{HNO}_3 \rightarrow 2 \text{H}_3\text{AsO}_4 + \text{N}_2\text{O}_3 \quad (2)$

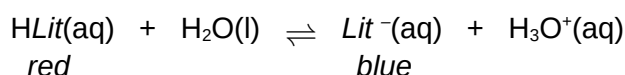
Question 27

(4 marks)

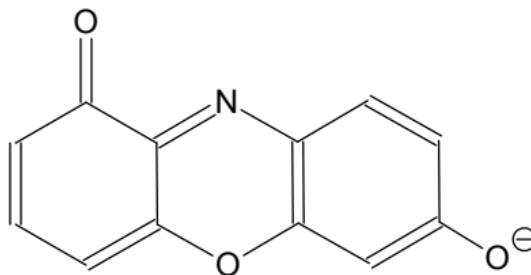
Litmus is a very common acid-base indicator which is extracted from lichens. It turns red in solutions that have a pH below 7 and blue when the pH is above 7. The substance responsible for the colour of litmus indicator is called 7-hydroxyphenoxazone. The structure of this molecule is shown below in its 'red form'.



A simplified way to express this molecule is HLit . This simplified notation is used in the equation below to demonstrate the reaction that litmus undergoes to change colour.



- (a) Explain how litmus indicator works. Include details of the colour change observed in acidic and basic solution. (3 marks)
- litmus works because the acidic / protonated form is a different colour (red) than the basic / deprotonated form (blue)
 - In acidic solution the reverse reaction is favoured due to presence of protons/hydrogen ions/hydronium ions and protonated ie. red form of litmus dominates
 - In basic solution the equilibrium shifts to the right due to the presence of hydroxide ions and the blue form dominates
- (b) Draw the 'blue form' of 7-hydroxyphenoxazone. (1 mark)

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

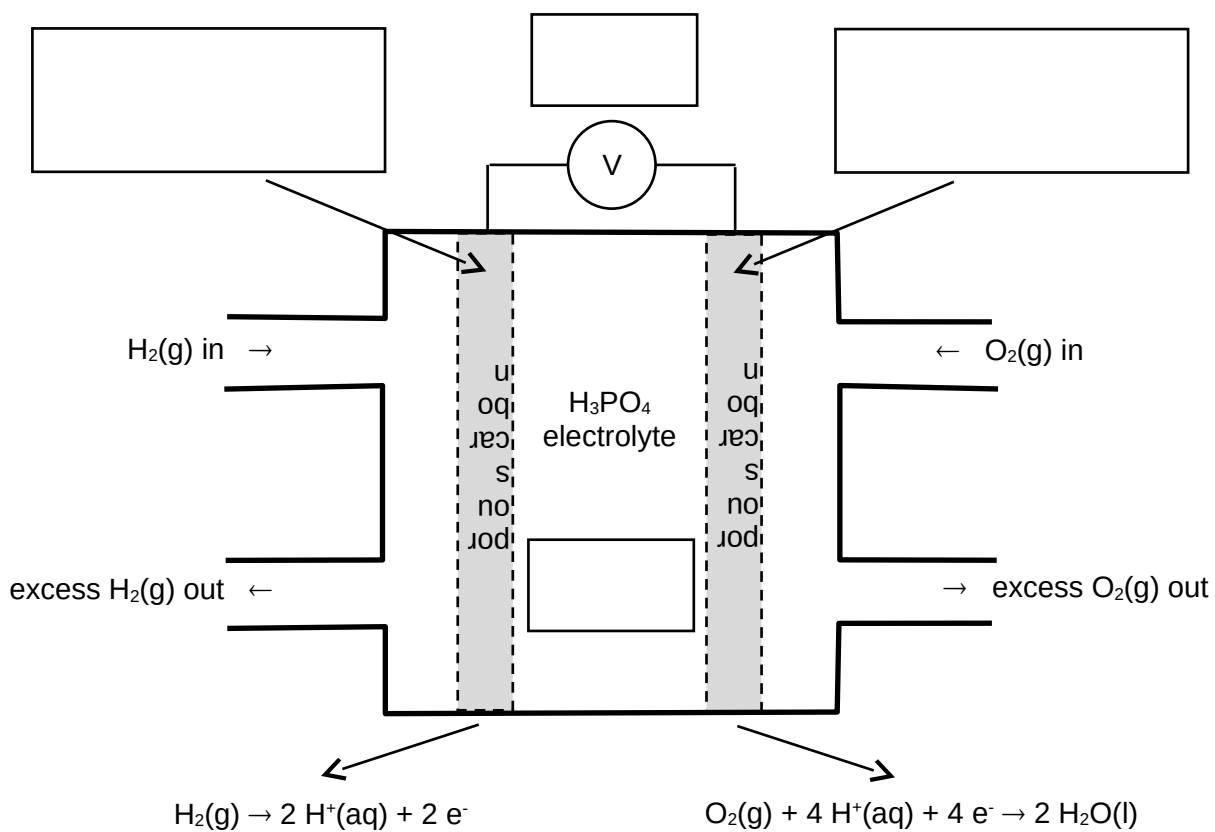
The phosphoric acid fuel cell (PAFC) uses gaseous oxygen and hydrogen to produce electricity. The cell is named so, because the electrolyte is an extremely concentrated solution of phosphoric acid. Both electrodes are made from porous carbon, which is coated with a platinum catalyst. The cell operates at temperatures of 150-210 °C and a single cell can produce a maximum of 1 volt, though most are in the range of 0.6-0.8 volts. PAFC's can be used to power buses and in stationary power generators. A simplified diagram of a PAFC is shown below.

Anode
-

$\rightarrow e^- \rightarrow$

Cathode
+

$\rightarrow \text{cations} \rightarrow$



- (a) What is the key difference between fuel cells and other galvanic cells? (2 marks)
- **fuel cells require a continuous input of reactants and therefore have the ability to produce a continuous voltage**
 - **other galvanic cells contain a fixed amount of reactant and once this is used up the cell will cease to produce a voltage**

- (b) In the boxes on the diagram above, label the;
- anode and cathode
 - charge of each electrode
 - direction of electron flow, and
 - direction of cation (H^+) flow.
- (4 marks)

- (c) Explain why many consider this fuel cell to be a 'clean' source of energy. Use a chemical equation to support your answer. (2 marks)

- **the only product of this cell reaction is water, completely harmless substance**
- **overall cell reaction: $2 H_2 + O_2 \rightarrow 2 H_2O$**

- (d) Describe how each of the gaseous reactants may be sourced. (2 marks)

Oxygen gas	Extracted from air
Hydrogen gas	By-product of crude oil processing / steam reforming / electrolysis of water

- (e) Why is the actual voltage produced by the PAFC different than the predicted value of 1.23 V calculated from the table of standard reduction potentials? (2 marks)

any 2 relevant points...

- **the cell described does not operate under standard conditions therefore SRPT cannot be used to predict voltage**
- **i.e. temp of 150-210 °C and use of extremely concentrated phosphoric acid**
- **some of the potential energy may be converted to heat**
- **ohmic loss; drop in voltage due to resistance of cell components**

Question 29

(9 marks)

Consider the following closed equilibrium system, which has been allowed to establish equilibrium at a temperature of 600 °C. The value of K for this reaction at 600 °C is 7.94×10^{-7} .



- (a) Write an equilibrium constant (K) expression for this reaction. (1 mark)

$$K = [\text{O}_2]$$

Some additional $\text{O}_2\text{(g)}$ is injected into this equilibrium system at 600 °C. The system was then allowed to re-establish equilibrium.

- (b) How has the mass of Cu(s) present changed in this new equilibrium? (circle) (1 mark)

increased

decreased

no change

- (c) At this new equilibrium, state the concentration of $\text{O}_2\text{(g)}$, in mol L^{-1} . Explain your answer. (2 marks)

- concentration of O_2 is $7.94 \times 10^{-7} \text{ mol L}^{-1}$
- since temperature has not changed, the value of K has not changed; value of K only depends on concentration of O_2 , therefore concentration of O_2 must have readjusted back to original level

- (d) A small amount of $\text{Cu}_2\text{O(s)}$ was then added to this equilibrium system. Explain how this would effect the equilibrium position. (2 marks)

- no effect
- solids have no measurable 'concentration' so addition or removal of a solid has no impact on equilibrium

- (e) At 800 °C, the value of K for this reaction is 3.16×10^{-5} . What does this tell you about the enthalpy change (ΔH) for this reaction? Explain your answer. (3 marks)

- the value of K has increased which indicates more products are present
- this means the forward reaction must be favoured with the addition of heat
- therefore the forward reaction is endothermic, ie ΔH is positive

Question 30**(9 marks)**

Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is an organic acid, found in high levels in foods such as almonds, banana, rhubarb and spinach. It is a weak, diprotic acid which has many uses in the laboratory, such as in volumetric analysis where it can be used as a primary standard.

- (a) Explain what is meant when oxalic acid is referred to as a 'weak, diprotic acid'. Use relevant chemical equations to support your answer. (4 marks)

- 'weak' indicates ionisation of oxalic acid does not go to completion
- 'diprotic' indicates each molecule of oxalic acid contains 2 ionisable/acidic hydrogen atoms
- $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{H}_3\text{O}^+$ OR $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{H}^+$
- $\text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{O}_4^{2-} + \text{H}_3\text{O}^+$ OR $\text{HC}_2\text{O}_4^- \rightleftharpoons \text{C}_2\text{O}_4^{2-} + \text{H}^+$

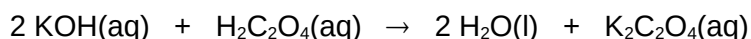
Some oxalic acid dihydrate crystals were used to produce a primary standard for use in a titration. 4.434 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ was dissolved in water and made up to 250.0 mL in a volumetric flask.

- (b) Calculate the concentration of the oxalic acid primary standard. (2 marks)

$$\begin{aligned} n(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}) &= m/M \\ &= 4.434 / 126.068 \\ &= 0.0351715 \text{ mol} \end{aligned}$$

$$\begin{aligned} c(\text{H}_2\text{C}_2\text{O}_4) &= n/V \\ &= 0.0351715 / 0.2500 \\ &= 0.140686 \text{ mol L}^{-1} \\ &= 0.1407 \text{ mol L}^{-1} \text{ (4SF)} \end{aligned}$$

The oxalic acid solution was then used to standardise some aqueous potassium hydroxide. A 20.00 mL sample of $\text{KOH}(\text{aq})$ required 17.85 mL of oxalic acid to reach equivalence. The relevant chemical equation for the titration is shown below.



- (c) Calculate the concentration of $\text{KOH}(\text{aq})$. (3 marks)

$$\begin{aligned} n(\text{H}_2\text{C}_2\text{O}_4) &= cV \\ &= 0.140686 \times 0.01785 \\ &= 0.0025112 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{KOH}) &= 2 \times n(\text{H}_2\text{C}_2\text{O}_4) \\ &= 0.0050225 \text{ mol} \end{aligned}$$

$$\begin{aligned} c(\text{KOH}) &= n/V \\ &= 0.0050225 / 0.02000 \\ &= 0.251124 \text{ mol L}^{-1} \\ &= 0.2511 \text{ mol L}^{-1} \text{ (4SF)} \end{aligned}$$

Question 31**(6 marks)**

Two beakers contained separate samples of zinc bromide solution, $\text{ZnBr}_2(\text{aq})$. To one beaker a piece of tin metal, $\text{Sn}(\text{s})$, was added. To the second beaker a piece of magnesium metal, $\text{Mg}(\text{s})$, was added. In one beaker, a reaction took place, while in the other beaker no reaction was observed.

- (a) Which of these metals (i.e. magnesium or tin) is the strongest reducing agent? Explain your answer. (2 marks)

- **Magnesium**
- **E° value of oxidation of magnesium is 2.36 V compared to 0.14 V for tin, therefore a stronger tendency to be oxidised and thus a stronger reducing agent. E° -ve**

- (b) Write a balanced chemical equation for the reaction that does occur, and explain why no reaction is observed in the other beaker. (2 marks)

- **$\text{Mg}(\text{s}) + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Zn}(\text{s})$**
OR
- **$\text{Mg}(\text{s}) + \text{ZnBr}_2(\text{aq}) \rightarrow \text{MgBr}_2(\text{aq}) + \text{Zn}(\text{s})$**
- **No reaction observed with tin metal as Sn^{2+} has a higher reduction potential than Zn^{2+} / Sn^{2+} is a stronger oxidant than Zn^{2+} / Zn is a stronger reductant than Sn**

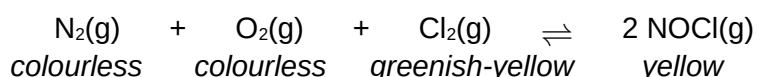
Some chlorine water, $\text{Cl}_2(\text{aq})$, was added to a separate third sample of zinc bromide solution.

- (c) Explain what would occur when these solutions were mixed. Include in your answer the expected observations. (2 marks)

- **a halogen displacement reaction would occur**
- **pale yellow and colourless solutions would mix to produce an orange solution**

Question 32**(8 marks)**

In the following equilibrium system, nitrogen, oxygen and chlorine gases combine to produce nitrosyl chloride vapour. This equilibrium system can form at temperatures of around 400 °C.



If an equal number of moles of $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ were injected into a sealed flask at 400 °C;

- (a) Explain what would happen to the forward and reverse reaction rates as the system moved to establish equilibrium. (3 marks)

- **the forward reaction rate would initially be high, as the molecules collide to produce NOCl, and would slowly decrease as the reactants form products**
- **the reverse reaction rate would initially be zero, but as NOCl is produced it would begin to increase**
- **at equilibrium the rate of forward and reverse reactions becomes equal**

- (b) Explain what would happen to the concentration of all gases as the system moved to establish equilibrium. (3 marks)

- **the concentration of N_2 , O_2 , and Cl_2 would all decrease**
- **the concentration of NOCl would increase from an initial concentration of zero**
- **the concentration of NOCl would increase by double the amount that $\text{N}_2/\text{O}_2/\text{Cl}_2$ decrease, in proportion with the stoic ratio 1:1:1:2**

- (c) Explain what you would observe as the system moved to establish equilibrium. (2 marks)

- **the greenish-yellow colour of the original mixture would become more yellow**
- **at equilibrium the colour of the system would be unchanging**

Question 33**(8 marks)**

Phosphate buffered saline (PBS) is a solution which is commonly used in biological research. It was specifically designed so that the ion concentrations of the buffer solution match those found in the human body. The table below gives a standard 'recipe' for making PBS. The four salts are dissolved in water to produce the concentrations indicated.

Salt	Final concentration when dissolved in distilled water	
	Conc. (g L ⁻¹)	Conc. (mmol L ⁻¹)
NaCl	8.0	137
KCl	0.2	2.7
Na ₂ HPO ₄	1.42	10
KH ₂ PO ₄	0.24	1.8

- (a) Which components would produce the buffering effect observed in PBS? Explain your answer. (2 marks)

- **Na₂HPO₄ and KH₂PO₄**
- **The HPO₄²⁻ / H₂PO₄⁻ are a weak conjugate acid-base pair**

- (b) Write an equation showing the buffering system that would form. (1 mark)

- **H₂PO₄⁻ + H₂O ⇌ HPO₄²⁻ + H₃O⁺ (B1)**
- OR**
- **H₂PO₄⁻ + OH⁻ ⇌ HPO₄²⁻ + H₂O (B2)**

- (c) Explain how this buffer is able to resist a change in pH when a small amount of NaOH(aq) is added. (2 marks)

- **The addition of NaOH neutralises the H₃O⁺ (B1) / increases the concentration of OH⁻ (B2)**
- **The system then favours the forward reaction to produce more H₃O⁺ (B1) / reduce the amount of OH⁻ (B2), thereby maintaining a constant pH**

PBS is specially designed for use in molecular biology and microbiology labs, so it is made to particular specifications.

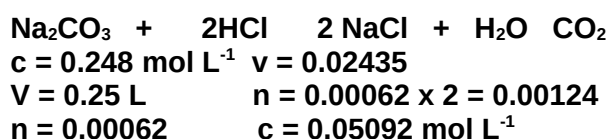
- (d) Define 'buffering capacity' and describe how you could increase the buffering capacity of PBS if you did not have to take into account its biological uses. (3 marks)

- **buffering capacity is the extent to which a buffer can maintain a constant pH when additional H₃O⁺ or OH⁻ is being added**
- **the buffering capacity of PBS could be increased by combining the HPO₄²⁻ / H₂PO₄⁻ in equimolar amounts, and**
- **by increasing the concentration of both HPO₄²⁻ / H₂PO₄⁻**

Question 34**(9 marks)**

A student set out to compare the effectiveness of a given quantity of two antacid preparations, one containing $\text{Mg}(\text{OH})_2$ and the other $\text{Al}(\text{OH})_3$, purchased from his local pharmacy. He titrated each preparation against a hydrochloric acid solution to determine how much acid each could neutralise and to determine the concentration of active ingredient in each preparation. He first standardised the hydrochloric acid solution available in the laboratory against a primary standard, and chose anhydrous sodium carbonate as the primary standard.

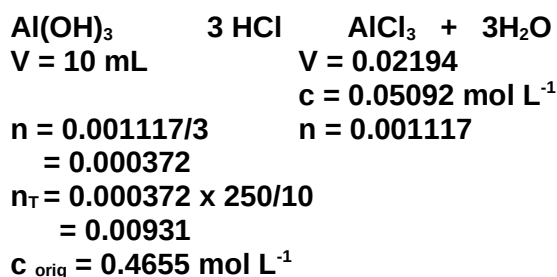
- (a) The student prepared 1.00 L of a $0.0248 \text{ mol L}^{-1} \text{Na}_2\text{CO}_3$ solution. He titrated three 25.0 mL aliquots of this solution against the HCl and found an average titre of 24.35 mL. Calculate the concentration of the standardised HCl solution. (4 marks)



- (b) The antacid suspensions were thoroughly shaken and 20.0 mL of each transferred to separate 250.0 mL volumetric flasks. Both were made up to the mark with distilled water and shaken vigorously. 10.0 mL aliquots of the diluted suspensions were transferred to conical flasks for titration and an appropriate indicator added. The titre values obtained for the $\text{Al}(\text{OH})_3$ suspension are shown in the table below:

Titre volume HCl (mL)				Average titre volume (mL)
Trials				
1	2	3	4	
22.62	21.98	21.94	21.90	21.94

Calculate the concentration, in moles per litre (mol L^{-1}), of $\text{Al}(\text{OH})_3$, in the original $\text{Al}(\text{OH})_3$ suspension. (5 marks)



End of Section Two

Section Three: Extended answer**40% (80 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.

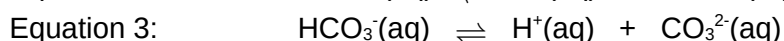
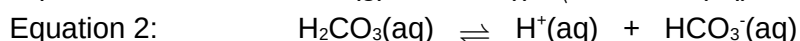
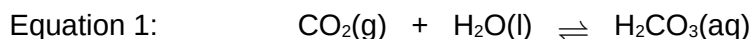
Spare pages are included at the end of this booklet. They can be used for planning your responses and/or as additional space if required to continue an answer.

- Planning: If you use the spare pages for planning, indicate this clearly at the top of the page.
- Continuing an answer: If you need to use the space to continue an answer, indicate in the original answer space where the answer is continued, i.e. give the page number. Fill in the number of the question(s) that you are continuing to answer at the top of the page.

Suggested working time: 70 minutes.

Question 35**(12 marks)**

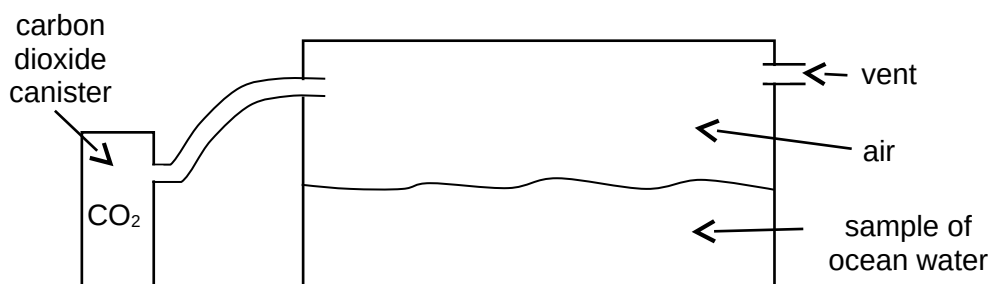
For the last few decades, the climate change debate has been taking place between the scientists, governments, companies and citizens of our planet. Rising carbon dioxide levels are thought to have contributed significantly to this climate change, including the phenomenon known as 'ocean acidification'. Some of the chemistry behind carbon dioxide and its link to ocean acidification is represented in the equations below.



One of the many negative consequences of ocean acidification is thought to be the disruption of the chemistry of ocean water, leading to things such as a decreased rate of calcification amongst many marine organisms. For example, one of the main compounds from which coral build their structure is calcium carbonate. Ocean acidification decreases the amount of calcium carbonate available to these organisms and thereby severely impacts their survival. This has already been observed in the Great Barrier Reef and many countries are already committed to reducing their nation's carbon dioxide emissions in an effort to combat the climate change we are witnessing.

- (a) Explain how an increase in atmospheric carbon dioxide, $\text{CO}_2(\text{g})$, levels can cause a change in the pH of our oceans. (3 marks)
- **Some atmospheric carbon dioxide dissolves in ocean water to produce the weak carbonic acid (equation 1)**
 - **The carbonic acid then ionises to produce H_3O^+ (equation 2 and 3)**
 - **Since $\text{pH} = -\log[\text{H}_3\text{O}^+]$, the presence of additional H_3O^+ in our oceans lowers the pH and causes acidification**

A chemistry teacher was attempting to demonstrate the process of ocean acidification to her class using the apparatus shown in the diagram below. A sample of ocean water was placed in a glass fish tank and a canister of carbon dioxide was attached by a tube. When the canister was opened, additional carbon dioxide gas was introduced into the air in the fish tank. A small vent ensured the overall air pressure in the fish tank remained constant.



- (b) Explain, in terms of the collision theory and with reference to Equation 1, the effect on both the forward and reverse reaction rates, when the partial pressure of $\text{CO}_2(\text{g})$ present in the tank was increased. (3 marks)

- as the partial pressure of CO_2 is increased, this increases the rate of collision between CO_2 and H_2O (Equation 1), increasing the forward reaction rate significantly (1)
- the production of more H_2CO_3 molecules then also causes the reverse reaction rate to increase (1)
- as the system moves to establish equilibrium, the forward reaction rate will decrease and the reverse reaction rate will increase, until they are again equal; however at the new equilibrium, both reaction rates will be higher than original

Note: not an actual equilibrium so marks allocated for collision discussion

- (c) Does the teacher's demonstration represent an open or closed equilibrium system? Explain. (2 marks)

- open
- matter (i.e. CO_2) is being added into the system (and air is able to leave)

- (d) State two (2) negative consequences associated with a decreased calcification rate amongst marine organisms such as coral. (2 marks)

- any 2 consequences... species may become threatened / populations of calcifying organisms may decline or die out / coral reefs become damaged / marine organisms which shelter in coral reefs may be at risk / sources of food may be removed from ecosystems / coastlines become less protected without the coral reefs etc

- (e) Australia recently committed to reducing its carbon dioxide emissions 26% by the year 2030. Other than reducing the effects of ocean acidification, state and explain one other benefit this might produce for our climate. (2 marks)

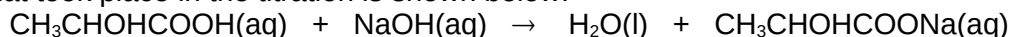
- may prevent further increase in global surface temperatures
- carbon dioxide is a greenhouse gas which traps heat and is thought to contribute to global warming

Question 36**(17 marks)**

- (a) Explain why phenolphthalein indicator is used. Use a chemical equation to support your answer. (3 marks)

- **the equivalence point of this titration is basic**
- **due to the production of the basic salt $\text{CH}_3\text{CHOHCOONa}$**
- **$\text{CH}_3\text{CHOHCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CHOHCOOH} + \text{OH}^-$**

A cheese maker added 4.00 L of milk to a small sample of bacterial culture. He knew that once the concentration of lactic acid reached $1.25 \times 10^{-2} \text{ mol L}^{-1}$ the cheese would be ready. He took a 10.00 mL sample of the whey, added several drops of phenolphthalein, and titrated the sample against a 0.111 mol L^{-1} NaOH solution. 1.15 mL of NaOH was required for equivalence. The reaction that took place in the titration is shown below.



- (b) Determine the concentration of lactic acid in the whey, and comment on whether or not the cheese maker should allow the reaction to proceed for longer before isolating the curds. (4 marks)

$$\begin{aligned} n(\text{NaOH}) &= cV \\ &= 0.111 \times 0.00115 \\ &= 1.2765 \times 10^{-4} \text{ mol (1)} \\ n(\text{CH}_3\text{CHOHCOOH}) &= n(\text{NaOH}) \\ &= 1.2765 \times 10^{-4} \text{ mol (1)} \\ c(\text{CH}_3\text{CHOHCOOH}) &= n/V \\ &= 1.2765 \times 10^{-4} / 0.01000 \\ &= 1.2765 \times 10^{-2} \text{ mol L}^{-1} \\ &= 1.28 \times 10^{-2} \text{ mol L}^{-1} \text{ (3SF) (1)} \end{aligned}$$

reaction should be stopped now as concentration of lactic acid is $> 1.25 \times 10^{-2} \text{ mol L}^{-1}$ (1)

- (c) Determine the percent by mass of lactic acid present in the whey at this point in time, if the 10.00 mL sample was taken from a total volume of 3.10 L of whey. The density of the whey is 1.040 kg L^{-1} . (5 marks)

$$\begin{aligned} n(\text{CH}_3\text{CHOHCOOH in 3.10 L}) &= cV \\ &= 1.2765 \times 10^{-2} \times 3.1 \\ &= 0.0395715 \text{ mol} \\ m(\text{CH}_3\text{CHOHCOOH}) &= nM \\ &= 0.0395715 \times 90.078 \\ &= 3.56452 \text{ g} \\ m(\text{whey}) &= V \\ &= 1.040 \times 3.10 \\ &= 3.224 \text{ kg} \\ &= 3224 \text{ g} \\ \% \text{ lactic acid in whey} &= 3.56452 / 3.224 \times 100 \\ &= 0.11056 \% \\ &= 0.111 \% \text{ (3SF)} \end{aligned}$$

- (d) The cheese maker only took one 10.00 mL sample of whey to examine, but he could have performed multiple trials of the titration if he had wished. Explain how this would improve the accuracy of his calculated lactic acid concentration. (2 marks)

- **repeat trials allow an average titre to be calculated rather than one single value**
- **averaging data reduces the effects of random errors on the results and improves reliability**

Another cheese maker mistakenly used methyl orange indicator in an identical titration.

- (e) Would he have obtained a smaller or larger NaOH titre reading? Comment on whether this is a random or systematic error. Explain your answer. (3 marks)

- **his titre value would have been smaller (resulting in a lower calculated lactic acid concentration)**
- **systematic error that is -error was in the method used by the scientist,(could have been prevented) would have given consistently low titre values, accuracy can be improved by altering the method i.e. indicator**

Question 37

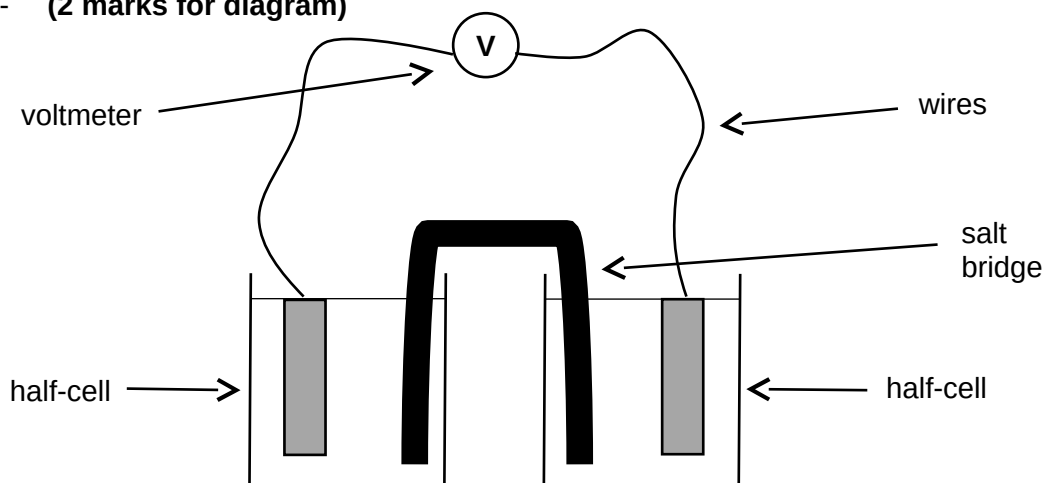
(13 marks)

A group of chemistry students were asked to carry out an investigation. They were given three different standard half-cells as follows;

- A nickel electrode in a solution of 1.0 mol L^{-1} nickel nitrate, i.e. $\text{Ni} / \text{Ni}^{2+}(\text{aq})$
- A silver electrode in a solution of 1.0 mol L^{-1} silver nitrate, i.e. $\text{Ag} / \text{Ag}^{+}(\text{aq})$
- A lead electrode in a solution of 1.0 mol L^{-1} lead(II) nitrate, i.e. $\text{Pb} / \text{Pb}^{2+}(\text{aq})$

(a) Describe how you could experimentally determine which of these three half-cells could be used to produce an electrochemical cell with the maximum possible voltage/EMF. You may assume you have access to standard laboratory equipment. Include a sketch of your apparatus. (5 marks)

- use a salt bridge, wires and voltmeter to;
- connect the half-cells to each other in pairs until all three combinations have been done (i.e. Ni & Ag, Ni & Pb, Ag & Pb)
- record the values of the voltage produced by each to find the highest
- (2 marks for diagram)



(b) Assuming standard conditions, what results would you expect? Give your answer in the form of a table displaying the predicted EMF values. (4 marks)

	EMF / voltage produced
Ni/Ni²⁺ // Pb²⁺/Pb	0.11 V
Ni/Ni²⁺ // Ag⁺/Ag	1.04 V
Pb/Pb²⁺ // Ag⁺/Ag	0.93 V

(3) for correct values
(1) for neat labelled table with units

(c) Briefly describe the chemical principles behind an electrochemical cell and explain why different cells are able to produce different voltages. (4 marks)

any 4 relevant points...

- electrochemical cells use a redox reaction where the oxidation (loss of electrons) happens in a physically different location to the reduction (gain of electrons)
- the electrons are forced to divert through an external pathway to move from the reductant to the oxidant, and this creates an electrical current
- different voltages are produced by different cells because oxidation and reduction half-reactions have different E^0 values i.e. varying tendencies to be reduced or oxidised
- the greater the difference in the E^0 value of the two half-reactions involved, the greater the voltage produced by the cell
- cells may also be connected in series to produce a larger range of voltages

Question 38

(19 marks)

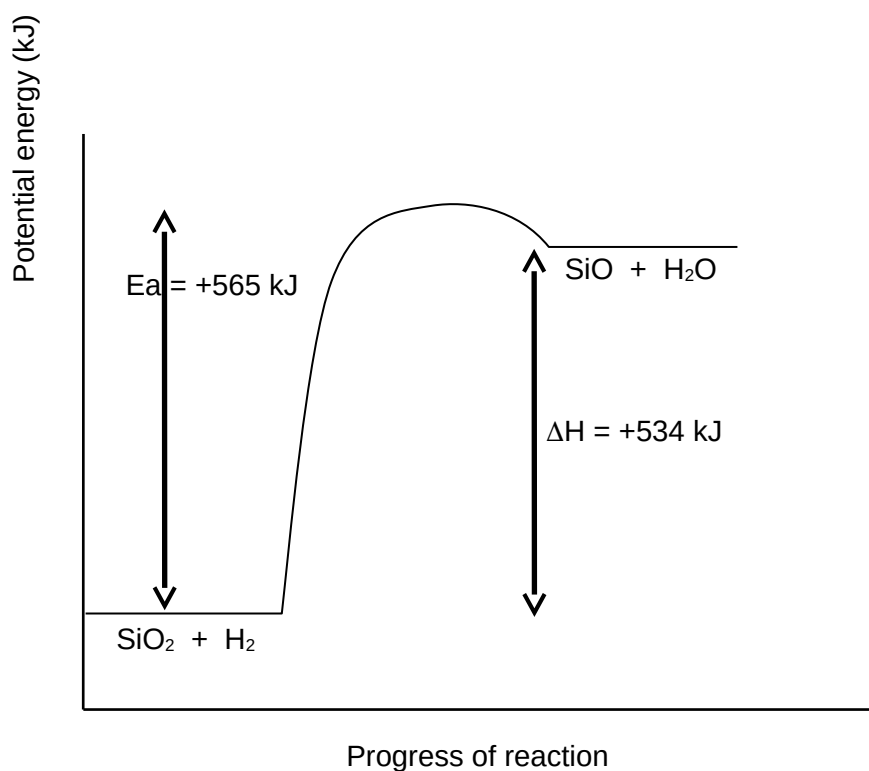
Silicon dioxide (SiO_2) is one of the most abundant substances in the Earth's crust. It is most commonly found in quartz and many types of sand and because of this, is often found in metal ores that are mined from the Earth's crust. One of the methods that can be used to remove silicon dioxide from an ore is illustrated in the equation below.



This chemical equation represents the equilibrium that forms between silicon dioxide and silicon monoxide. The activation energy for this reaction is 565 kJ mol^{-1} .

- (a) Identify the oxidising agent (oxidant) and reducing agent (reductant) in this reaction. Use oxidation numbers to support your answer. (2 marks)
- **SiO_2 is the oxidant; O.N. of Si changes from +4 to +2**
 - **H_2 is the reductant; O.N. of H changes from 0 to +1**
- (b) Draw an energy profile diagram for this reaction. Label the activation energy and the enthalpy change. (4 marks)

- | |
|------------------------|
| 1- Shape |
| 1- endo |
| 1- E_a labelled |
| 1- ΔH labelled |



(c) Determine the value of;

(2 marks)

$E_a(\text{rev})$ **31 kJ mol^{-1}** $\Delta H(\text{rev})$ **-534 kJ mol^{-1}**

Quite a low pressure, around atmospheric, is used for this process. However a high temperature of 1550°C is maintained in the reaction chamber.

- (d) Explain, in terms of the collision theory, the effect of each of the following on reaction rate. (5 marks)

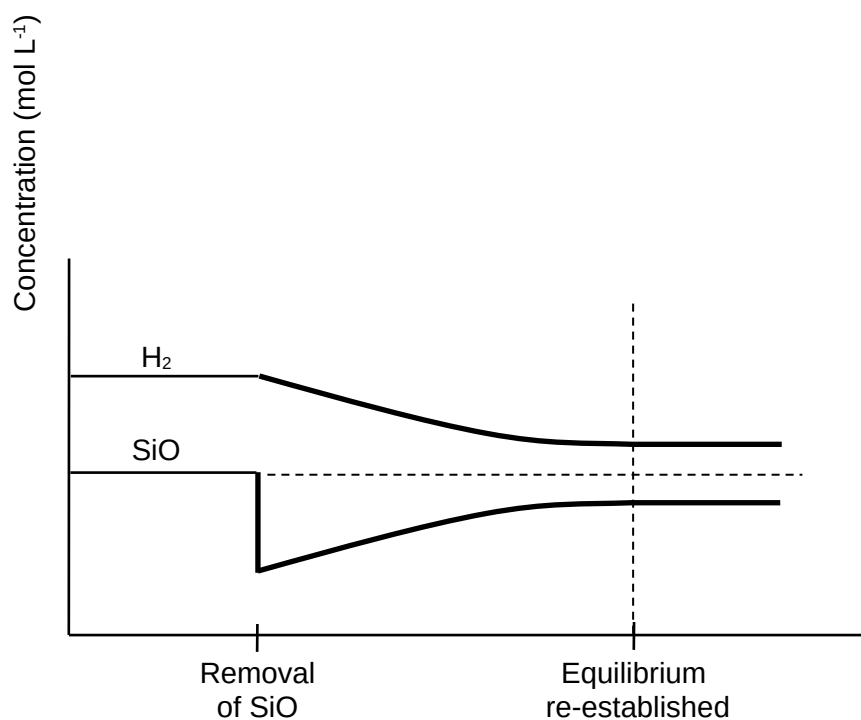
Use of high temperature	<ul style="list-style-type: none">- increases average kinetic energy of reactants and results in an increased number of collisions- also a greater proportion of reacting species have sufficient energy to overcome E_a barrier- therefore a faster reaction rate
Use of low pressure	<ul style="list-style-type: none">- decreases number of collisions that occur between reactants due to large distances between gas particles- therefore a slower reaction rate

- (e) State the effect (increased, decreased or no change) of each of the following on yield. (2 marks)

Use of high temperature	increased
Use of low pressure	increased

Since the silicon monoxide is produced in gaseous form, SiO(g) , it is easily removed from the system. This in turn helps to favour the forward reaction.

- (f) Continue the concentration graph below, by sketching the effect of removing a batch of SiO(g) from the reaction chamber. (4 marks)



- (1) steep drop in SiO
- (1) lines should curve in correct direction
- (1) lines should have the same shape (reduction in H₂ approx. same as increase in SiO)
- (1) SiO should not return to original levels
- (1) lines should be parallel at equilibrium

-1 mark for each mistake

Question 39**(19 marks)**

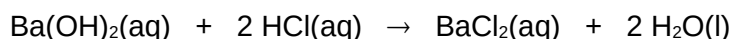
Barium hydroxide, $\text{Ba}(\text{OH})_2(\text{s})$, also known as 'baryta' is often found in hydrated form and appears as white crystals. It is corrosive, toxic and moderately soluble in water. It can be used in titrations, for the manufacture of organic substances, as well as in the synthesis of other barium-containing compounds.

A barium hydroxide solution was made by dissolving 1.31 g of solid anhydrous $\text{Ba}(\text{OH})_2$ crystals into 795 mL of water.

- (a) Calculate the pH of this solution. (5 marks)

$$\begin{aligned}
 n(\text{Ba}(\text{OH})_2) &= m/M \\
 &= 1.31 / 171.316 \\
 &= 7.64669 \times 10^{-3} \text{ mol} \\
 \\
 c(\text{Ba}(\text{OH})_2) &= n/V \\
 &= 7.64669 \times 10^{-3} / 0.795 \\
 &= 9.61848 \times 10^{-3} \text{ mol L}^{-1} \\
 \\
 c(\text{OH}^-) &= 2 \times c(\text{Ba}(\text{OH})_2) \\
 &= 0.019237 \text{ mol L}^{-1} \\
 \\
 [\text{H}^+] &= 1.0 \times 10^{-14} / [\text{OH}^-] \\
 &= 1.0 \times 10^{-14} / 0.019237 \\
 &= 5.19833 \times 10^{-13} \text{ mol L}^{-1} \\
 \\
 \text{pH} &= -\log[\text{H}^+] \\
 &= -\log(5.19833 \times 10^{-13}) \\
 &= 12.2841 \\
 &= 12.3 \text{ (3SF)}
 \end{aligned}$$

This solution of barium hydroxide was then neutralised by the addition of hydrochloric acid, $\text{HCl}(\text{aq})$, as shown in the equation below.



- (b) Davy was one of the first chemists to study the composition of hydrochloric acid. Briefly state the main developments he made in the field of acid-base theory. (2 marks)

any 2 relevant points...

- **it was previously thought that acids must contain oxygen and therefore 'oxides' were all acidic**
- **demonstrated HCl was composed of hydrogen and chlorine**
- **proposed that acids must contain hydrogen**
- **(also accept 'proposed that acids contain replaceable hydrogen' as this is stated in the Unit 3 syllabus, however this was an extension of Davy's theory made by Von Leibig, not actually proposed by Davy himself)**

- (c) Using the same equation, explain how it relates to the definition of an acid and a base as proposed by Arrhenius, and why it is that these two substances are able to neutralise each other. (3 marks)

- **according to Arrhenius; acids are substances that contain H in their formula and produce H^+ ions in solution (i.e. HCl fits definition)**
- **bases are substances that have OH in their formula and produce OH^- ions in solution (i.e. $\text{Ba}(\text{OH})_2$ fits definition)**
- **they are able to neutralise each other because $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$**

Hydrocyanic acid, $\text{HCN}(\text{aq})$, is an extremely poisonous acid with a K_a value of 6.17×10^{-10} . It is made by dissolving liquid or gaseous hydrogen cyanide in water. Small amounts of hydrogen cyanide can be extracted from the stones of some fruits such as cherries, apricots and apples, however it is generally manufactured on an industrial scale.

- (d) Write two (2) equations for the ionisation of HCN in water, one illustrating the Arrhenius theory and one the Bronsted-Lowry theory. (2 marks)

Arrhenius	$\text{HCN}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CN}^-(\text{aq})$
Bronsted-Lowry	$\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$ <div style="text-align: center;"> <p>A B CA CB</p> </div>

- (e) On the Bronsted-Lowry equation above, label the conjugate acid-base pairs. (2 marks)

- (f) What information does the value of K_a give us about hydrocyanic acid, $\text{HCN}(\text{aq})$? Explain your answer. (2 marks)

- tells us that HCN is a weak acid i.e. ionisation of HCN does not occur to a large extent
- since K is equivalent to P/R , very low K value indicates that there is a much higher concentration of reactants present at equilibrium i.e. unionised HCN

The Bronsted-Lowry theory accounts for the acidic and basic properties of a much wider array of substances whose properties cannot be explained by earlier theories.

- (g) Complete the following table by stating the pH and giving a supporting equation for each of the substances. (3 marks)

Substance	pH (acidic, basic or neutral)	Equation
$\text{MgS}(\text{aq})$	basic	$\text{S}^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HS}^-(\text{aq}) + \text{OH}^-(\text{aq})$
$\text{NH}_3(\text{aq})$	basic	$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
$\text{KHSO}_4(\text{aq})$	acidic	$\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

End of questions