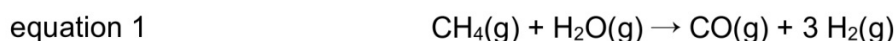1 With climate change being one of the 21st century's most pressing problems, efforts have been made to track the amount of greenhouse gases released into the atmosphere.

(a) The Haber Process produces ammonia, which can be processed further into fertilisers for crops to grow.

This process requires the use of hydrogen gas, $H_2(g)$, which is not abundant in the atmosphere. Instead, $H_2(g)$ is produced industrially through a few reactions described in equations 1 to 3. Overall in this process, 7 moles of methane used results in 2 moles of oxygen consumed.

equation 1	$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3 H_2(g)$
equation 2	$2 CH_4(g) + O_2(g) \rightarrow 2 CO(g) + 4 H_2(g)$
equation 3	$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

For the following questions in (a), assume that the processes in which hydrogen gas is produced are 100% efficient.

(i) Carbon monoxide, $CO(g)$, is a poisonous gas. Plants producing hydrogen gas avoid the release of $CO(g)$ into the atmosphere.

Calculate the mass of $CO_2(g)$ released into the atmosphere per gram of ammonia produced. [3]

We need to construct an overall equation for the process where no $CO(g)$ is produced. However, we may find many possible ways to add up equations 1, 2 and 3 together such that in the overall equation, no $CO(g)$ is the product. However, 7 moles of methane used results in 2 moles of oxygen consumed. This motivates us to add up 3 moles of equation 1, 2 moles of equation 2, and thus 7 moles of equation 3 (to cancel out the $CO(g)$ terms). The resultant equation is:

$3 CH_4(g) + 3 H_2O(g) + 4 CH_4(g) + 2 O_2(g) + 7 H_2O(g) \rightarrow 9 H_2(g) + 8 H_2(g) + 7 CO_2(g) + 7 H_2(g)$
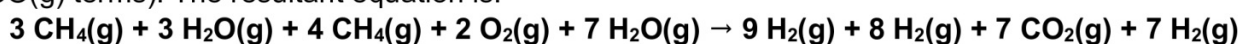
Simplifying this equation we get $7 CH_4(g) + 10 H_2O(g) + 2 O_2(g) \rightarrow 24 H_2(g) + 7 CO_2(g)$

7 moles of $CO_2(g)$ is produced per 24 moles of $H_2(g)$, and per 24 moles of $H_2(g)$, 16 moles of $NH_3(g)$ is produced ($N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$).

Therefore, the mass of $CO_2(g) = \dfrac{1}{14.0 + 3(1.0)} \times \dfrac{7}{16} \times (12.0 + 2(16.0)) = 1.13$ g

(ii) $O_2(g)$ and $N_2(g)$ has a ratio of close to 1:4 in the atmosphere. Show that air from the atmosphere used to provide $O_2(g)$ in equation 2 contains almost the right amount of $N_2(g)$ to react with $H_2(g)$ produced from equations 1 to 3. [2]

From (i), $7 CH_4(g) + 10 H_2O(g) + 2 O_2(g) \rightarrow 24 H_2(g) + 7 CO_2(g)$
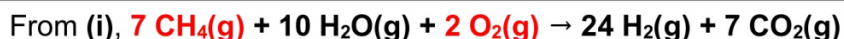
For every 2 moles of $O_2(g)$, there is 8 moles of $N_2(g)$.

1 mole of $N_2(g)$ reacts with 3 moles of $H_2(g)$ to form ammonia. The ratio of $N_2(g)$ to $H_2(g)$ is 8:24 = 1:3. Hence, air from the atmosphere used to provide $O_2(g)$ contains the stoichiometric amount of nitrogen to react with hydrogen produced.

(iii) Environmental activists have been calling for the reduction of the emissions of greenhouse gases in the atmosphere. Actions such as flying less will help to cut carbon dioxide emissions.

The Haber process accounts from approximately 3% of $CO_2(g)$ worldwide, almost the same as the aviation industry.
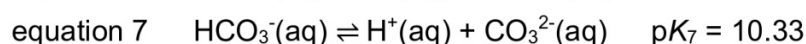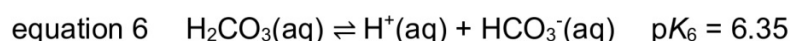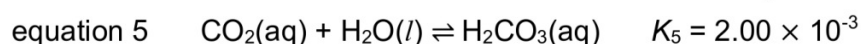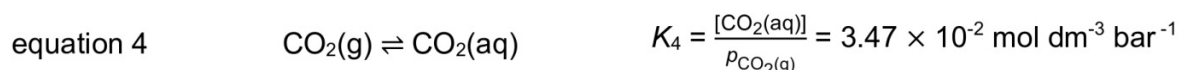
Suggest why the Haber Process **cannot** be discontinued although it produces a lot of greenhouse gases. [1]

Ammonia is an essential component of fertilisers, which are important in growing crops to feed us.
Accept any reasonable answer that implies that the Haber process is extremely important and essential to our survival.

$CO_2(g)$ has many adverse effects on the environment. Apart from trapping heat, ecosystems are also affected with heightened levels of $CO_2(g)$.

When $CO_2(g)$ is absorbed into the ocean, the pH of seawater will decrease.

The following equilibria exist in seawater. All values are quoted at 25 degrees Celsius.

equation 4 $CO_2(g) \rightleftharpoons CO_2(aq)$ $K_4 = \frac{[CO_2(aq)]}{p_{CO_2(g)}} = 3.47 \times 10^{-2}$ mol dm^{-3} bar^{-1}

equation 5 $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ $K_5 = 2.00 \times 10^{-3}$

equation 6 $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $pK_6 = 6.35$

equation 7 $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $pK_7 = 10.33$

Shells that protect living things in the ocean contain $CaCO_3(s)$ which is an essential building block. $CaCO_3(s)$ is in equilibrium with the ocean's water as described by equation 8.

equation 8 $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

(b) **(i)** Suggest how a decrease in the pH levels of seawater results in less calcium being present in shells produced by living creatures. [2]

(explanation for why) A decrease in the pH levels of water results in less free CO_3^{2-} ions.
A higher $[H^+]$ results in the position of equilibrium of equation 7 to shift left to counteract the increase in $[H^+]$, this consuming CO_3^{2-} ions.

A drop in $[CO_3^{2-}]$ results in the position of equilibrium of equation 8 to shift right. This releases more $CaCO_3(s)$ into the water. Thus shells contain less $CaCO_3(s)$ and less Ca.

(ii) Calculate the concentration of carbonate ions in seawater given that the atmosphere contains 0.04% of CO_2(g) by amount and that the pH of seawater is 8.10. [2]

We can find the equilibrium constant of the equation $CO_2(g) + H_2O(g) \rightleftharpoons 2\,H^+(aq) + CO_3^{2-}(aq)$
to be $K = K_4K_5K_6K_7 = 3.47 \times 10^{-2} \times 2.00 \times 10^{-3} \times 10^{-6.35} \times 10^{-10.33} = 1.450 \times 10^{-21}$ mol^3 dm^{-9} bar^{-1}

$$[CO_3^{2-}] = \frac{K \times p_{CO_2}}{[H^+]^2} = \frac{1.450 \times 10^{-21} \times \frac{0.04}{100} \times 1.01325}{\left(10^{-8.10}\right)^2} = 9.31 \times 10^{-9} \text{ mol dm}^{-3}$$

Note that atmospheric pressure is 1.01325 bar.

(iii) In Singapore, the decrease in pH of seawater is around 0.06 units from 1700 to 1990. However, in the same period at the coasts of Greenland, Norway, Sweden and Iceland, the decrease in pH is around 0.11.

By comparing the climates of the 2 regions in the above-mentioned information, deduce the sign of enthalpy change of the dissolution of CO_2(g) into water. [2]

Singapore's climate is warmer, while Greenland's, Norway's, Sweden's and Iceland's climate is colder on average. Since there's a larger drop in pH of seawater for a colder climate, more dissolution of CO_2(g) occurred. **This means that the dissolution of CO_2(g) is exothermic.** The position of equilibrium (for the dissolution of CO_2(g)) shifts more to the right in a colder climate to generate more heat in response to the lower temperatures.

(c) It is hard to harvest the potential of CO_2(g) in the atmosphere due to its thermodynamic stability. This can be attributed to the strong C=O bond in CO_2(g).

Write a balanced equation with state symbols whose enthalpy change gives the bond energy of the C=O bond in CO_2(g). [1]

$$\frac{1}{2}\,CO_2(g) \rightarrow \frac{1}{2}\,C(g) + O(g)$$
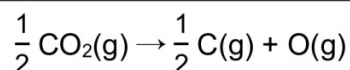
The coefficient of half is needed as we are looking at the average bond energy of both C=O bonds.

(d) Methane is a much more potent greenhouse gas than CO_2 as it is able to trap more heat. However, methane has a shorter lifespan in the atmosphere than CO_2. This limits its potency as a greenhouse gas since it has a shorter time to retain heat.

The main mechanism involved in the natural removal of methane in the atmosphere is through the reactive hydroxyl radical ($\cdot$OH). Equation 9 shows the elementary step in which methane reacts with the hydroxyl radical.

equation 9 $\qquad\qquad\qquad\qquad CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O$

(i) Write a rate equation for equation 9. [1]

rate = $k[CH_4][\cdot OH]$ (accept partial pressure variant)

(ii) Explain, in terms of oxidation numbers, whether equation 9 is a redox reaction. [1]

Oxidation numbers of C in CH_4 and $\cdot CH_3$ are -4 and -3 respectively, while oxidation numbers of O in $\cdot OH$ and H_2O are -1 and -2 respectively. Since $\cdot OH$ is reduced and CH_4 is oxidised, equation 9 is a redox reaction.

(iii) By assuming that the concentration of hydroxyl radicals, $[\cdot OH]$, is constant, express the half-life of CH_4 in terms of the rate constant of equation 9 and $[\cdot OH]$. [1]

The half-life of methane is given by

$$t_{\frac{1}{2}} = \frac{\ln 2}{k[\cdot OH]}$$

(iv) As $\cdot OH$ is extremely reactive, it is slowly depleted after an extended period of time. $\cdot OH$ reacts with other molecules such as carbon monoxide.

State the effect of a depleting source of hydroxyl radicals on the half-life of CH_4. [1]

The half-life of methane increases.

(v) Suggest why experts warn that an increase in the emission of methane will make methane harder to remove in the future. Hence, suggest why delaying action to reduce methane emissions will result in the methane being more potent as a greenhouse gas. [2]

With an increasing concentration of methane, the $\cdot OH$ gets depleted faster. This increases the half-life of methane, thus making methane harder to be removed as it is removed slower and remains longer in the atmosphere.

The longer we take to reduce methane emissions, the $\cdot OH$ gets depleted to a larger extent.

This is a good scientific argument to advocate for reducing methane emissions.

[Total: 19]

2 Antoine-Laurent Lavoisier is a French Scientist during the 1770s to 1780s. He is known to have created a revolution in Chemistry and has shaped our understanding of stoichiometry and oxidation.

During the 17th and 18th century, it is thought that combustion can be explained by the "Phlogiston Theory". The "Phlogiston Theory" stipulates that all things that can be burnt contain a certain amount of "phlogiston". When burnt, "phlogiston" is released to the atmosphere. Lavoiser disproved the "Phlogiston Theory" through a series of experiments and observations he made on his own.

(a) (i) Lavoisier observed that phosphorous readily combusts in air. This resulted in the phosphorous to gain weight.

Write a balanced equation for this process. [1]

$P_4 + 5\,O_2 \rightarrow P_4O_{10}$
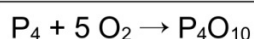
(ii) Explain how Lavoisier's observation contradicts the "Phlogiston Theory". [1]

The fact that phosphorous gained weight proves that "phlogiston" isn't released. If it is indeed released, then "phlogiston" has a negative mass, which is impossible (or we will expect phosphorous to lose mass which isn't the case.

(iii) In 1774, an English philosopher Joseph Priestley described how he heated mercury calx and collected a gas in which a candle burnt vigorously. Priestley believed this pure air is free of "phlogiston". He called this gas he obtained from mercury calx "dephlogisticated air". Suggest an identity for mercury calx. [1]
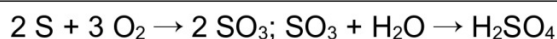
HgO or Hg_2O
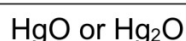
(iv) In 1779, Lavoisier announced to the Royal Academy of Sciences in Paris that he found that most acids contain this "dephlogisticated air". He called it "oxygène"—in Greek this means "acid generator".

Explain, with the aid of balanced chemical equations, how oxygen is able to generate an acid from
  • elemental sulfur, and
  • elemental aluminium. [3]

$2\,S + 3\,O_2 \rightarrow 2\,SO_3$; $SO_3 + H_2O \rightarrow H_2SO_4$
Sulfur trioxide may be hydrolysed by water to form sulfuric acid.

$4\,Al + 3\,O_2 \rightarrow 2\,Al_2O_3$; $Al_2O_3 + 2\,NaOH + 3\,H_2O \rightarrow 2\,Na[Al(OH)_4]$
Aluminum oxide reacts with a base like NaOH, thus aluminum oxide is an acid.

(b) Adulterated tobacco during Lavoisier's time was a serious issue. Tobacco would be mixed with ash and water. Ash, in particular, enhanced the smell of tobacco.

Lavoisier created a method to detect adulterated tobacco. "When a spirit of vitriol, *aqua fortis* (nitric acid) or some other acid solution is poured on ash, there is an immediate very intense effervescent reaction, accompanied by an easily detected noise."

(i) The gas from the effervescent reaction forms a precipitate in limewater. State the identity of the gas. [1]

CO_2

(ii) Hence, state the species in ash that is responsible for the "intense effervescent reaction". [1]

CO_3^{2-} or HCO_3^{2-}

(iii) Suggest why this species you identified in **(ii)** is found in ash. [1]

The carbon will be oxidised to its <u>highest oxidation state</u> of +4. This may exist in the form of CO_3^{2-} or HCO_3^{2-} as an ion.

(iv) "Vitriol" is a class of chemical compounds comprising of metal sulfates. Some solutions of "vitriol", such as aluminium sulfate or iron(III) sulfate, produced a positive result.

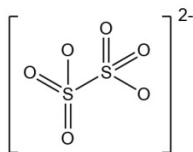Explain why such solutions of "vitriol" produce a positive result. [2]

The high charge density of the aluminum or iron(III) centre results in the O—H bond in the H_2O ligand being highly polarised and weakened. Thus, the $[Al(H_2O)6]^{3+}$ ion will partially dissociate to form free H^+ ions which then react with carbonate to form carbon dioxide.

[Total: 11]

3 The dithionate ion ($S_2O_6^{2-}$) is a stable sulfur oxoanion with a single S—S bond. Strong oxidants oxidise them to sulfates.

(a) State the oxidation state of sulfur in the dithionate ion, and draw the structure of the dithionate ion. In your structure, indicate the geometry about the sulfur atom, and a predicted bond angle. [3]

Oxidation state: +5
Geometry: Tetrahedral
Bond angle: 109.5 degrees

$$\left[\begin{array}{c} \overset{\displaystyle O}{\underset{\displaystyle O}{\underset{\|}{O=S}}} \; \overset{\displaystyle O}{\underset{\displaystyle O}{S=O}} \end{array} \right]^{2-}$$

At 75 degrees Celsius, the dithionate ion can be oxidised in acidic solutions. Preliminary experiments have suggested that the rate of reaction is directly proportional to the concentration of H^+ and $S_2O_6^{2-}$. The order of reaction with respect to the oxidising agent, however, is zero, while the rate constant for the oxidation of the dithionate ion by any oxidising agent is 2.56×10^{-5} dm^3 mol^{-1} s^{-1}. The rate of reaction is the rate of depletion of the dithionate ion.

An experiment was carried out to investigate the reduction of periodate ions by an excess of dithionate ions at 75 degrees Celsius. The periodate ions exist in the form $H_4IO_6^-$.

In this reaction, 2 successive stages were observed. In the first stage, periodate ions were reduced to elemental iodine. In the second stage, elemental iodine was further reduced.

The absorbance of the solution at a wavelength of 465 nm was monitored over a period of 40 minutes. The results are summarised in a graph in Fig 7.1. The absorbance of the solution is directly proportional to the concentration of elemental iodine.
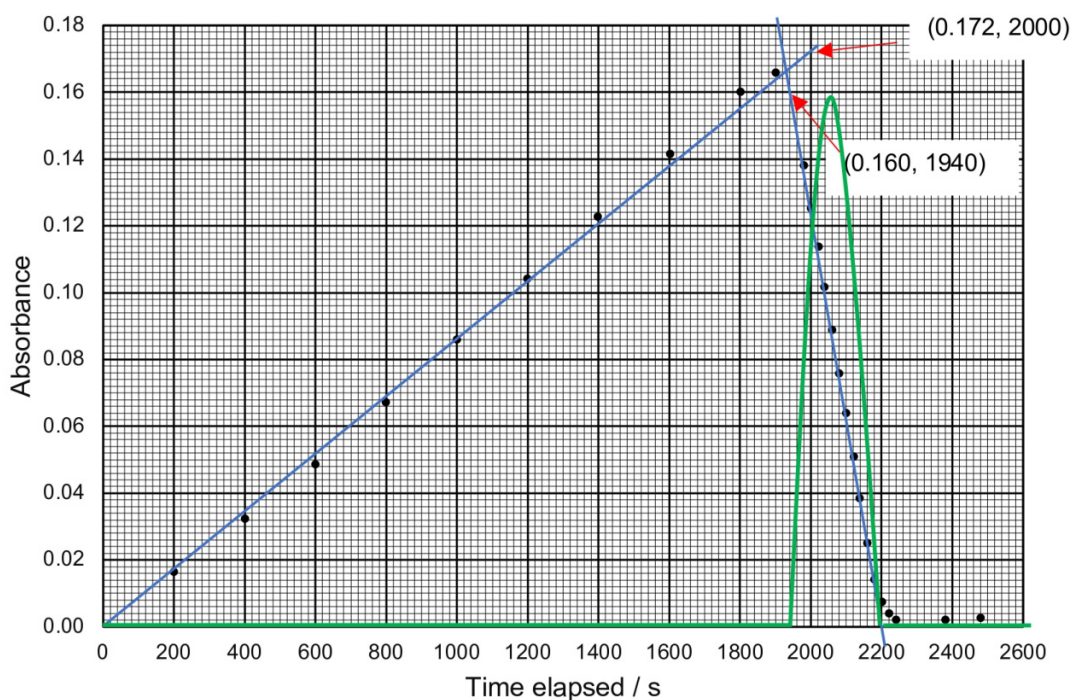

Fig 7.1

(b) (i) Showing your working clearly, construct balanced equations for stages 1 and 2. **[3]**

(1): $S_2O_6^{2-} + 2 H_2O \rightarrow 2 SO_4^{2-} + 4 H^+ + 2 e^-$ (the oxidation state of S increases from +5 to +6)

(2): $2 H_4IO_6^- + 14 e^- + 16 H^+ \rightarrow I_2 + 12 H_2O$ (the oxidation state of I decreases from +7 to 0)

(3): $I_2 + 2 e^- \rightarrow 2 I^-$ (this is for stage 2, which states that elemental iodine is further reduced)

Stage 1 is given by $7\times(1) + (2)$
This yields $7 S_2O_6^{2-} + 2 H_2O + 2 H_4IO_6^- \rightarrow I_2 + 12 H^+ + 14 SO_4^{2-}$

Stage 2 yields $S_2O_6^{2-} + 2 H_2O + I_2 \rightarrow 2 SO_4^{2-} + 4 H^+ + 2 I^-$

As implied in the question, acidic conditions should be used. You may use the method of balancing oxidation numbers instead of constructing half eqations.

(ii) State **two** pieces of evidence from Fig 7.1 that suggests that the order of reaction with respect to the periodate ion for stage 1 is zero. Explain your answer. **[2]**

Evidence 1: A best-fit straight line can be drawn through the points.
Evidence 2: This best-fit straight line passes through the origin.

The concentration of $[I_2]$ is directly proportional to time, meaning that the rate is constant and independent of the concentration of the periodate ion.

(iii) Explain the shape of graph in Fig 7.1. **[2]**

Increasing absorbance as I_2 is produced first. Decreasing absorbance as I_2 is consumed later. Since the rate of reaction with respect to the oxidant is zero, both lines are straight. (Not required to comment about the steepness of the lines in light of mark allocation)

(c) The initial conditions for the experiment are listed below:
- $[H_4IO_6^-] = 5.30 \times 10^{-4}$ mol dm^{-3}
- $[S_2O_6^{2-}] = 0.0519$ mol dm^{-3}
- $[H^+] = 0.728$ mol dm^{-3}

(i) When will you expect maximum absorbance to be recorded? **[2]**

Maximum concentration of elemental iodine is $5.30 \times 10^{-4} \times \frac{1}{2} = 2.65 \times 10^{-4}$ mol dm^{-3}.

Rate of production of elemental iodine (which is constant) = $k[S_2O_6^{2-}][H^+]$
$= \frac{1}{7} \times 2.56 \times 10^{-5} \times 0.0519 \times 0.728 = 1.3818 \times 10^{-7}$ mol dm^{-3} s^{-1}

Time when maximum absorbance is recorded = $\frac{2.65\times10^{-4}}{1.3818\times10^{-7}} = 1920$ s

Take note of how rate is defined, rate = rate of depletion of thionate ions. You will need to apply mole ratios to find the rate of production of elemental iodine.

For the upward sloping line, the line must pass through the origin since it is a zero-order kinetics behaviour.

(ii) Draw **two** best fit straight-lines that captures the trend of the graph in Fig 7.1. [1]

(iii) Calculate the magnitude of the gradient of both lines. [1]

Magnitude of gradient of upward sloping line = $\frac{0.172}{2000}$ = 8.60 × 10^{-5}

Magnitude of gradient of downward sloping line = $\left| \frac{0.160 - 0}{1940 - 2200} \right|$ = 6.1538 × 10^{-4} = 6.15 × 10^{-4}

Positive numbers should be given, as the question asked for the magnitude. Remember to leave your answer to 3 s.f.

(iv) <mark>To the nearest integer</mark>, state the ratio of the magnitude of the gradient of the steeper line to that of the gentler line. [1]

$$\frac{6.1538 \times 10^{-4}}{8.60 \times 10^{-5}} = 7$$

(v) Explain the significance of your answer in **(iv)** with reference to your answer in **(b)(i)**. [2]

In stage 2, iodine is reduced 7 times as fast (than it is produced in stage 1) as it takes only one-seventh of the dithionate ions to reduce iodine as compared to that in stage 1 where dithionate ions reduce periodate ions.

This is because the difference in the oxidation state of iodine in periodate to elemental iodine is 7, which is 7 times that of the difference in the oxidation state of iodine in elemental iodine and the iodide ion.

If the ratio of your gradients isn't 7, it is hard to account for the precise ratio of 7.
To arrive at this answer, you should think in terms of the consumption of dithionate ions first.
The consumption of dithionate ions is constant no matter the oxidizing agent!

(d) A further investigation of the reaction between iodine and dithionate ions was conducted. A large excess of dithionate and acid was present. A graph of the absorbance of the solution at 2 different wavelengths, 350 nm and 465 nm, against the time elapsed, t, is presented in Fig 7.2.
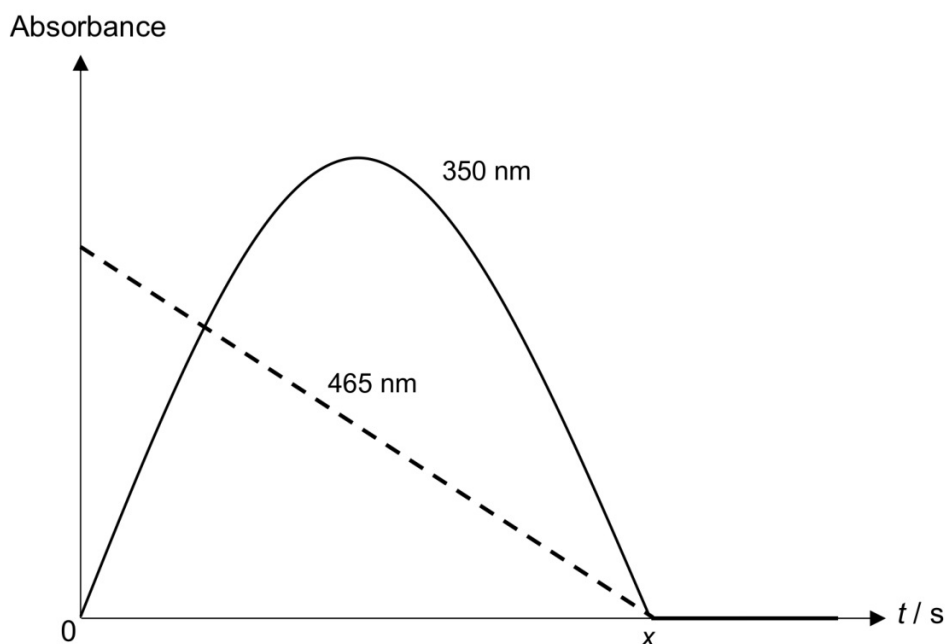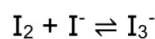

Fig 7.2

The absorbance at 350 nm is proportional to the concentration of triiodide, I_3^-, while the absorbance at 465 nm is proportional to the concentration of iodine. Triiodide ions are formed from the equilibrium between iodine and iodide ions, according to equation 7.1. The equilibrium constant for equation 7.1 is K.

equation 7.1 $\qquad\qquad\qquad\qquad\qquad\qquad$ $I_2 + I^- \rightleftharpoons I_3^-$

The order of reaction with respect to iodine is zero.

(i) Explain why at any point of time during the reaction, the relationship holds: $\qquad$ [1]

$$2\,[I_2]_{initial} = 2\,[I_2] + [I^-] + 3\,[I_3^-].$$

Once elemental iodine is reacted, it may exist in the form of elemental iodine, iodide or triiodide ions. The LHS and RHS account for the number of iodine atoms in each iodine-containing species. The coefficients 2 and 3 are used because there are 2 iodine atoms and 3 iodine atoms in elemental iodine and triiodide ions respectively.

The concentration of triiodide ions is negligible to the terms $[I_2]$ and $[I^-]$. You may assume for subsequent parts, $2\,[I_2]_{initial} = 2\,[I_2] + [I^-]$.

(ii) Express $[I_2]$ and $[I^-]$ in terms of $[I_2]_{initial}$, t, and v. v is the rate of loss of iodine. [1]

$[I_2] = [I_2]_{initial} - vt$
$[I^-] = 2vt$ (the coefficient 2 is used as 2 moles of iodide are produced per mole of elemental iodine reacted)

(iii) Hence, show that $[I_3^-]$ is a quadratic function of t. Show clearly that the roots of this quadratic function are 0 and x, the time where $[I_2]$ first reaches 0. [3]

$[I_3^-] = K [I_2] [I^-] = K ([I_2]_{initial} - vt)(2vt) = 2Kvt([I_2]_{initial} - vt) = 2Kv^2t^2 - 2Kvt [I_2]_{initial}$

$t = 0$ is a root. Also, since v is the rate of consumption of I_2, v is the magnitude of the gradient of the $[I_2]$ vs t graph. Hence, $[I_2]_{initial} = vx$ and $t = x$ is also a root.

During stage 1, no triiodide ions are present because no iodide ions are produced. In stage 2, the graph is a parabola (start and end of stage 2). Then the graph flattens at absorbance = 0. The height of the peak of the parabola doesn't matter too much. (**Line in green**)

(iv) In Fig 7.1, add in a line that illustrates the absorbance at 365 nm with respect to time. Label your graph clearly. [2]

[Total: 24]

4 Semiconductors are essential to our everyday lives. An understanding of how semiconductors work is crucial to new innovations and breakthroughs in the technology industry.

All materials have a valence band (VB) and a conductance band (CB). When enough energy is supplied, an electron in the VB becomes excited and promotes to the CB. The movement of electrons from the VB to the CB is what gives semiconductors conductivity.

When an electron (e^-) leaves the VB for the CB, a hole (h^+) is formed in the VB.

(a) Silicon is known to be a key element in many semiconductors. However, pure silicon is not considered to be a good semiconductor due to its low tendency to conduct electricity.

In pure silicon, a silicon atom forms four single covalent bonds with four other silicon atoms.

(i) Explain why silicon forms four covalent bonds. [1]

Silicon is in Group 14 and has 4 valence electrons. Forming 4 covalent bonds results in stable octet configuration being obtained.

(ii) Explain why silicon is a poor conductor of electricity. [1]

Silicon has a giant covalent structure and lacks delocalised electrons to act as charge carriers.

(iii) In a pure Group 14 semiconductor, electrons in the covalent bond are excited to the CB.

By examining a relevant property of a covalent bond, or otherwise, suggest why diamond is a poorer semiconductor than silicon. [1]

The Si—Si bond is weaker than the C—C bond. Hence, it is harder to break the C—C bond for the purpose of exciting an electron, subsequently diamond is a poorer semiconductor than carbon. (May also write about how tightly bound the valence electrons are to the nucleus)

Silicon can be doped with other elements to produce either a *n*-type or *p*-type semiconductor with increased conductivity.

Phosphorous doped (P-doped) silicon is a *n*-type semiconductor. A small fraction of silicon atoms is replaced with phosphorous atoms. However, phosphorous still forms four covalent bonds with four silicon atoms.

(iv) Draw a dot-and-cross diagram of a phosphorous atom in P-doped silicon. Include and differentiate electrons from the covalent bond phosphorous forms with silicon. (You do not need to include the silicon atoms in your answer.) [2]

Assume that the phosphorous atom only forms covalent bonds with silicon atoms only.

dots represent electrons from Si
crosses represent electrons from P
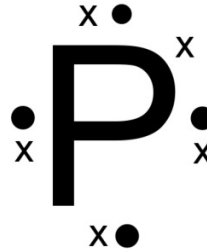
(v) Hence, explain why *n*-type semiconductors are said to have "extra electrons". [1]

Presence of additional unpaired electron from the P atom.

A *p*-type semiconductor is doped with other elements that give rise to "extra holes" in the semiconductor. Typically, there is 1 "extra hole" per atom.

(vi) Explain what element you will use to dope a germanium semiconductor that is *p*-type. [2]

A hole comes from the absence of an electron. Hence, we should dope germanium with a Group 13 element, like boron (any Group 13 element suffices). The absence of one electron in boron gives rise to a hole.

(b) The electrolysis of water produces hydrogen and oxygen gas. However, this process is not spontaneous. Many chemists are finding solutions to use renewable energy to electrochemically split water.

Semiconductors may act as photocatalysts to split water. One such semiconductor is TiO_2. When sunlight is irradiated onto TiO_2, a current (direction of flow indicated with the arrow) is generated. This is because photons from the sunlight excites the electrons in TiO_2.
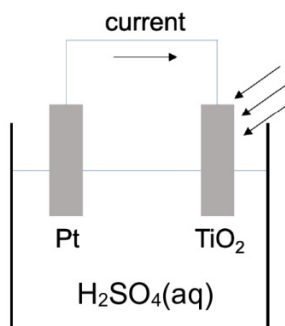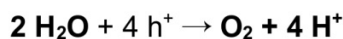

Fig 8.1

(i) Complete Table 8.2 below. [2]

electrode	Pt	TiO₂
type of electrode (circle one)	anode / **cathode**	**anode** / cathode
gas evolved at electrode	hydrogen	oxygen

Table 8.2

(ii) Complete the half equation for the TiO_2 electrode. [1]
(No electrons are involved in the half equation.)

$2 H_2O + 4 h^+ \rightarrow O_2 + 4 H^+$

(iii) The ratio of the number of carriers (electrons or holes) consumed in the water splitting reaction to the number of irradiated photons is called the quantum efficiency.

In one experiment lasting 100 seconds, 1.762×10^{20} photons are irradiated to give 5.00×10^{-6} mol of H_2. Calculate the quantum efficiency of the experiment. [2]

amount of electrons = $5.00 \times 10^{-6} \times 2 = 1.00 \times 10^{-5}$ mol
amount of photons = $1.762 \times 10^{20} \div (6.02 \times 10^{23}) = 2.9269 \times 10^{-4}$ mol

Quantum efficiency = $1.00 \times 10^{-5} \div (2.9269 \times 10^{-4}) \times 100\% = 3.42\%$

(iv) Referring to the experiment in **(iii)**, what is the average current recorded between the 2 electrodes? [1]

> $Q = nF = 1.00 \times 10^{-5} \times 96500 = 0.965$ C
> $I = Q/t = 0.965 \div 100 = 9.65 \times 10^{-3}$ A

(v) When TiO_2 is treated with H_2, TiO_{2-x} is formed. This is a partially reduced form of TiO_2. Suggest why TiO_{2-x} acts like a *n*-type semiconductor. [1]

> Reduction is the addition of electrons. Since TiO_{2-x} has extra electrons (in the form of Ti^{3+}), TiO_{2-x} acts like a n-type semiconductor.

(vi) What is the colour of TiO_2? Explain your answer. [2]

> White (reject colourless).
>
> Ti^{4+} has zero d electrons. Thus no d-d transition can occur, and no specific wavelength of light within the visible region is absorbed.

[Total: 17]