

## Data-based Questions (Physical Chemistry, Kinetics and Foundational Topics)

### Instructions for Practice

These questions are data-based questions. You need to apply your knowledge to novel scenarios.

Usually, each question has a theme. The theme for each question is listed here, but it will be explicitly listed in your exams.

In Paper 2, data-based questions will take up about 20 to 25 marks of the paper. You should allocate slightly more time to solve these data-based questions. The ideal time allocation for each question is 1.5 minutes per mark.

All questions in this set are original, and it is most likely that you will be seeing these questions for the first time.

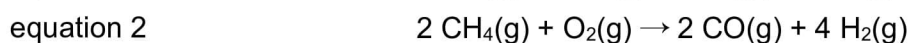
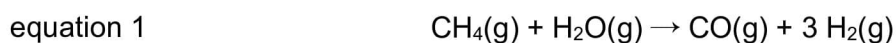
Happy revising!

Question number and Theme	Maximum Marks	Suggested time allocation
<b>1</b> Chemistry in the environment	19	34 minutes
<b>2</b> Chemistry before the 19 <sup>th</sup> century	11	16 minutes
<b>3</b> A study of the reaction between dithionate and periodate ions	24	40 minutes
<b>4</b> Semiconductors	17	28 minutes

1 With climate change being one of the 21<sup>st</sup> 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<sub>2</sub>(g), which is not abundant in the atmosphere. Instead, H<sub>2</sub>(g) is produced industrially from methane and water 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.



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<sub>2</sub>(g) released into the atmosphere per gram of ammonia produced. [3]

(ii) O<sub>2</sub>(g) and N<sub>2</sub>(g) has a ratio of close to 1:4 in the atmosphere. Show that air from the atmosphere used to provide O<sub>2</sub>(g) in equation 2 contains almost the right amount of N<sub>2</sub>(g) to react with H<sub>2</sub>(g) produced from equations 1 to 3. [2]

- (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<sub>2</sub>(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]

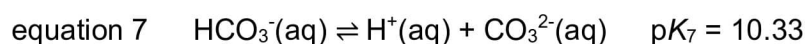
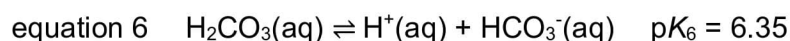
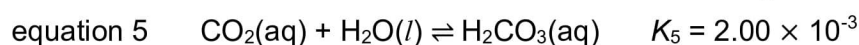
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CO<sub>2</sub>(g) has many adverse effects on the environment. Apart from trapping heat, ecosystems are also affected with heightened levels of CO<sub>2</sub>(g).

When CO<sub>2</sub>(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.



Shells that protect living things in the ocean contain CaCO<sub>3</sub>(s) which is an essential building block. CaCO<sub>3</sub>(s) is in equilibrium with the ocean's water as described by equation 8.



- (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]

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

- (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<sub>2</sub>(g) into water. [2]

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- (c) It is hard to harvest the potential of CO<sub>2</sub>(g) in the atmosphere due to its thermodynamic stability. This can be attributed to the strong C=O bond in CO<sub>2</sub>(g).

Write a balanced equation with state symbols whose enthalpy change gives the bond energy of the C=O bond in CO<sub>2</sub>(g). [1]

- (d) Methane is a much more potent greenhouse gas than CO<sub>2</sub> as it is able to trap more heat. However, methane has a shorter lifespan in the atmosphere than CO<sub>2</sub>. 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 ( $\cdot\text{OH}$ ). Equation 9 shows the elementary step in which methane reacts with the hydroxyl radical.

equation 9



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

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

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(iii) By assuming that the concentration of hydroxyl radicals, [ $\cdot\text{OH}$ ], is constant, express the half-life of  $\text{CH}_4$  in terms of the rate constant of equation 9 and [ $\cdot\text{OH}$ ]. [1]

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

State the effect of a depleting source of hydroxyl radicals on the half-life of  $\text{CH}_4$ . [1]

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(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]

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[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 17<sup>th</sup> and 18<sup>th</sup> 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. Lavoisier 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]

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(ii) Explain how Lavoisier’s observation contradicts the “Phlogiston Theory”. [1]

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(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]

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(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]

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- (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]

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

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

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- (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]

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[Total: 11]

3 The dithionate ion ( $\text{S}_2\text{O}_6^{2-}$ ) 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]

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  $\text{H}^+$  and  $\text{S}_2\text{O}_6^{2-}$ . 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  $2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . 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  $\text{H}_4\text{IO}_6^-$ .

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.

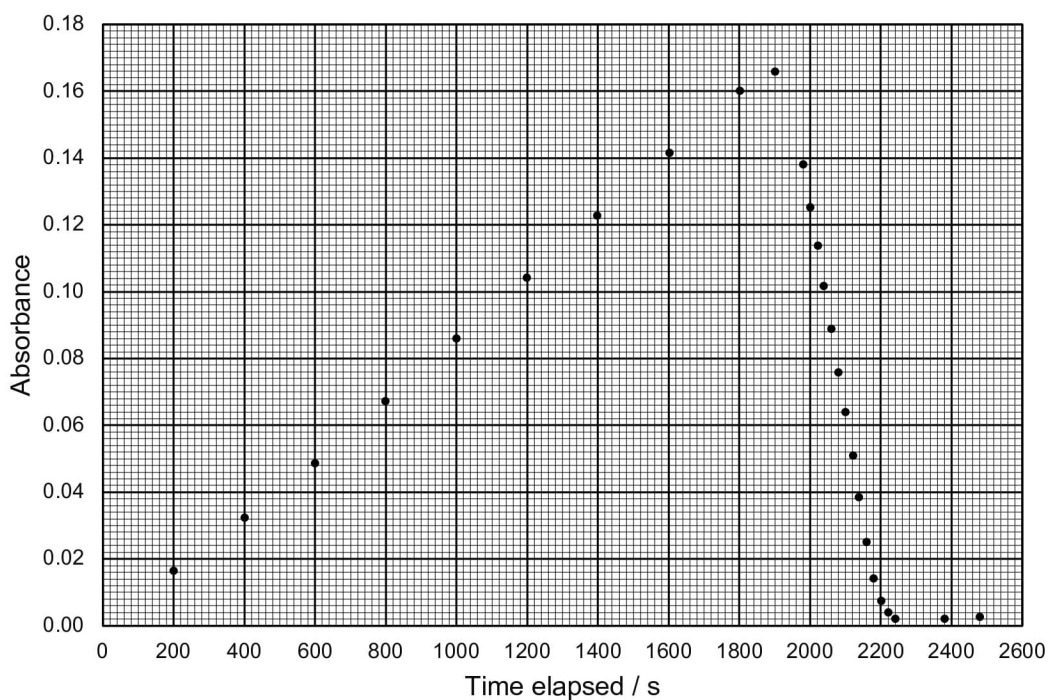


Fig 7.1



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

(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]

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

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(c) The initial conditions for the experiment are listed below:

- $[\text{H}_4\text{IO}_6^-] = 5.30 \times 10^{-4} \text{ mol dm}^{-3}$
- $[\text{S}_2\text{O}_6^{2-}] = 0.0519 \text{ mol dm}^{-3}$
- $[\text{H}^+] = 0.728 \text{ mol dm}^{-3}$

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

(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]

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

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

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*Question 3 continues on the next page.*

- (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.

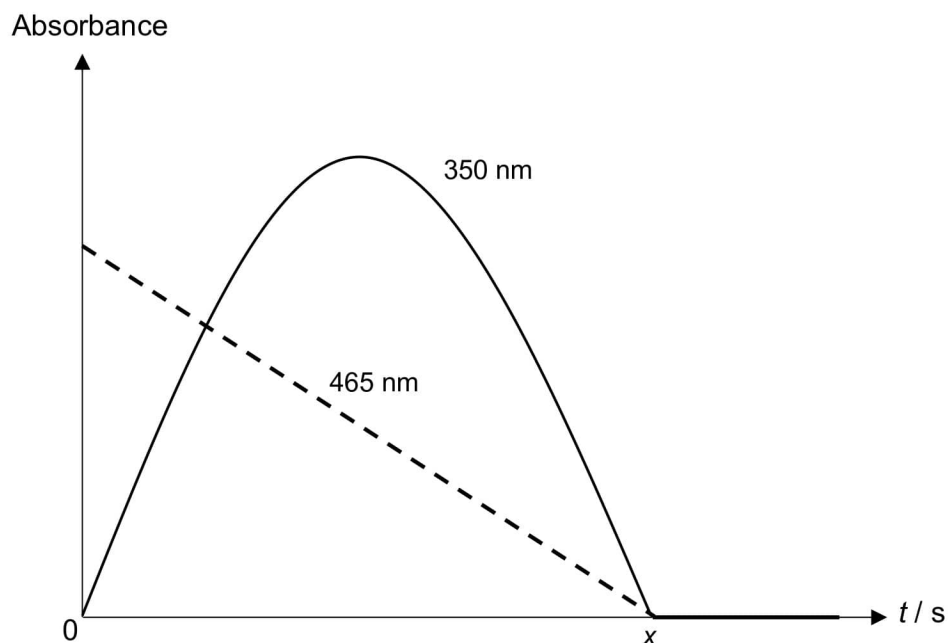
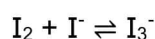


Fig 7.2

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



The order of reaction with respect to iodine is zero.

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

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

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

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

(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]

(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]

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

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- (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]

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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.

- (v) Hence, explain why *n*-type semiconductors are said to have “extra electrons”. [1]

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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]

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- (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  $\text{TiO}_2$ . When sunlight is irradiated onto  $\text{TiO}_2$ , a current (direction of flow indicated with the arrow) is generated. This is because photons from the sunlight excites the electrons in  $\text{TiO}_2$ .

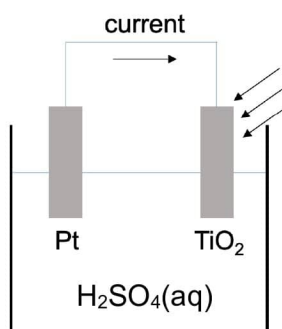


Fig 8.1

- (i) Complete Table 8.2 below. [2]

electrode	Pt	$\text{TiO}_2$
type of electrode (circle one)	anode / cathode	anode / cathode
gas evolved at electrode		

Table 8.2

- (ii) Complete the half equation for the  $\text{TiO}_2$  electrode.  
(No electrons are involved in the half equation.) [1]



- (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,  $1.762 \times 10^{20}$  photons are irradiated to give  $5.00 \times 10^{-6}$  mol of  $\text{H}_2$ . Calculate the quantum efficiency of the experiment. [2]

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

(v) When  $\text{TiO}_2$  is treated with  $\text{H}_2$ ,  $\text{TiO}_{2-x}$  is formed. This is a partially reduced form of  $\text{TiO}_2$ . Suggest why  $\text{TiO}_{2-x}$  acts like a *n*-type semiconductor. [1]

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(vi) What is the colour of  $\text{TiO}_2$ ? Explain your answer. [2]

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[Total: 17]