Section A

Answer **all** the questions in this section.

1 **(a)** Account for the reactions that occur when $MgCl_2$ and PCl_5 are separately dissolved in water. Predict the pH of the resulting solutions formed and write equations for the reactions that occur. [4]

(b) A sample consists of a solid mixture of MgO and Al_2O_3. Describe briefly an experimental procedure that will enable you to separate the mixture and recover each of the oxides in its pure form. [3]

(c) The highest fluoride of xenon, XeF_6, can be obtained by heating the octafluoroxenates of the Group 1 metals, M_2XeF_8, where M represents the Group 1 metal.

$$M_2XeF_8 \rightarrow 2MF + XeF_6$$

Suggest reasons why the sodium salt (M = Na) decomposes below 100 °C, whereas the caesium salt (M = Cs) requires a temperature of 400 °C. Hence explain why $MgXeF_8$ is not known to exist. [3]

(d) Suggest identities for the following substances **A** to **D**, writing equations where appropriate.

When magnesium is heated with nitrogen under inert conditions, an ionic compound, **A** is produced. When water is added to **A**, a colourless gas **B** which turns damp red litmus paper blue is produced. **B** reacts with chlorate(I) ion, ClO^- in a 2 : 1 mole ratio to form a colourless liquid **C** with empirical formula NH_2. The reaction of **C** with sulfuric acid in a 1:1 mole ratio produces a salt **D**, $N_2H_6SO_4$, which contains one cation and one anion per formula unit. [4]

(e) Real gases do not obey the ideal gas equation exactly. Many chemists have tried to come up with gas equations that describe the behaviour of real gases. In 1873 J D van der Waals introduced an approximate gas equation that is applicable for all real gases. The van der Waals equation is

$$P = \frac{nRT}{V - n\mathbf{b}} - \mathbf{a}\frac{n^2}{V^2}$$

where **a** and **b** are constants which are characteristic of each gas. The other symbols carry their usual meaning and units as in the ideal gas equation.

(i) Using what you have learnt about the differences between ideal and real gases, suggest what the constants **a** and **b** represent. [2]

(ii) The values of the constants **a** and **b** for CO_2 are **a** = 0.3658 Pa m^6 mol^{-2} and **b** = 4.29×10^{-5} m^3 mol^{-1}.

Use your answer in **(e)(i)** to suggest how the value of the constant **a** for xenon (Xe) will compare with CO_2. Explain your answer briefly. [1]

(iii) Use the
- ideal gas equation and
- van der Waals equation

to calculate the pressure exerted by 1 mol of CO_2 at a temperature of 30 °C and volume of 1 dm^3.

[3]
[Total: 20]

2 (a) Malonic acid, $CH_2(CO_2H)_2$ is an organic *weak dibasic acid*. It is a building block chemical to produce numerous valuable compounds, including the flavour and fragrance compound, cinnamic acid, and the pharmaceutical compound, valproate. The two pK_a values of $CH_2(CO_2H)_2$ are 2.83 and 5.69.

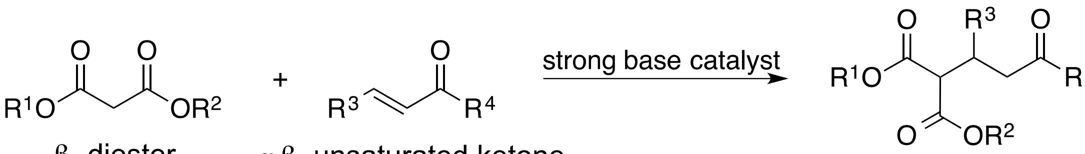
(i) Define the term *weak acid*. [1]

(ii) Calculate the pH of 25.0 cm^3 solution of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. [1]

(iii) Calculate pH of the resulting solution when 50 cm^3 of 0.100 mol dm^{-3} NaOH was added to the solution in **(a)(ii)**. [2]

(iv) Using your answers in **(a)(ii)** and **(a)(iii)**, as well as the pK_a values provided, sketch a graph to show how the pH of the solution changes as 50 cm^3 of 0.100 mol dm^{-3} NaOH is gradually added to 25.0 cm^3 of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. Clearly indicate the corresponding volumes of NaOH in your graph. [2]

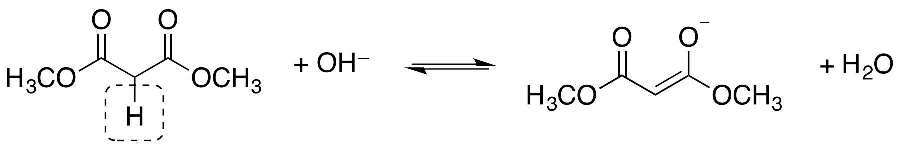
(b) Malonic acid can be converted to its corresponding β–diester. β–diesters are commonly used as starting compounds in the Michael addition reaction, where they react with α,β-unsaturated ketones. It is one of the most useful methods for the formation of C–C bonds.



β–diester α,β–unsaturated ketone

(i) Suggest reagents and conditions to convert malonic acid to dimethyl malonate, $CH_2(COOCH_3)_2$. State the type of reaction. [2]

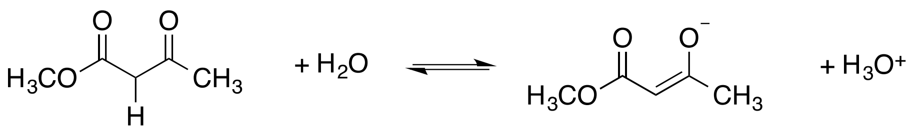
(ii) The first step in the mechanism of Michael addition involves an acid–base reaction where the strong base catalyst extracts an α-hydrogen from the β–diester.



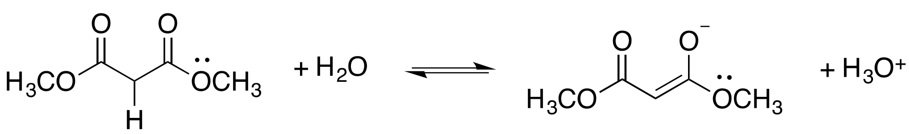
α-hydrogen

Reagents similar to the malonate ester can undergo the same type of reaction. The pK_a values of malonate ester and another similar reagent are as follows:

pKa



β-ketoester 11



β-diester 13

Explain the difference in pK_a values between the two compounds. [2]

(iii) Compound **A**, C_8H_9ClO, contains a non-aromatic six-membered ring. **A** reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent. 1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum. When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed. **B** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. When **B** is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed. **D** also gives a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.

Deduce the structural formulae of compounds **A**, **B**, **C**, **D** and **E**, explaining clearly your reasoning for all reactions described.

[10]
[Total: 20]

3 **(a)** A Latimer diagram provides a concise way of representing large amount of information about the different oxidation states of an element. In a Latimer diagram, the most highly oxidised form of an element is written on the left, with successively lower oxidation states to the right. The different species are connected by arrows, and the standard electrode potential in volts is written above each arrow.

The Latimer diagrams for chlorine in acidic and alkaline medium are shown below.

In acidic medium:

$$ClO_4^- \xrightarrow{+1.19\text{ V}} ClO_3^- \xrightarrow{+1.21\text{ V}} ClO_2^- \xrightarrow{+1.66\text{ V}} ClO^- \xrightarrow{+1.64\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

In alkaline medium:

$$ClO_4^- \xrightarrow{+0.36\text{ V}} ClO_3^- \xrightarrow{+0.35\text{ V}} ClO_2^- \xrightarrow{+0.65\text{ V}} ClO^- \xrightarrow{+0.40\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

(i) Define the term *standard electrode potential*. [1]

(ii) The standard electrode potentials in a Latimer diagram are not additive. For example, the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is **not** the sum of +1.19 V and +1.21 V and +1.66 V. However, their respective standard Gibbs' free energy changes are additive.

Using relevant data given below, show that the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is 1.34 V.

electrode reaction	$E^\ominus$ / V	$\Delta G^\ominus$ / kJ mol^{-1}
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–220.7
$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$	+1.21	–233.5
$ClO_2^- + 2H^+ + 2e^- \rightleftharpoons ClO^- + H_2O$	+1.66	–320.4
$ClO^- + 2H^+ + e^- \rightleftharpoons \frac{1}{2}Cl_2 + H_2O$	+1.64	–158.3
$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36	–131.2

[2]

(iii) With the exception of the conversion of Cl_2 to Cl^-, the standard electrode potentials in alkaline medium are less positive than their corresponding conversions in the acidic medium.

Suggest why this is so. [2]

(iv) A disproportionation reaction is a redox reaction in which a chemical species undergo reduction and oxidation simultaneously.

In hot alkaline medium, Cl_2 undergoes disproportionation to form two chlorine-containing species according to the following equation.

$$3Cl_2(g) + xOH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_y^-(aq) + zH_2O(l)$$

By considering the number of moles of electrons transferred and using the Latimer diagram for chlorine in alkaline medium, first solve for y. Then, use it to solve for x and z. [2]

(b) Besides the standard hydrogen electrode, other reference electrodes have also been employed in electrochemistry. An example is the silver chloride electrode, which involves dipping silver metal coated with solid silver chloride into a solution of sodium chloride. The solubility product for $AgCl$ is 2.0×10^{-10} $mol^2\ dm^{-6}$.

(i) The standard electrode potential of a silver chloride electrode is +0.230 V. However, when 1.0 mol dm^{-3} sodium chloride is used to set up the silver chloride electrode, this value cannot be achieved.

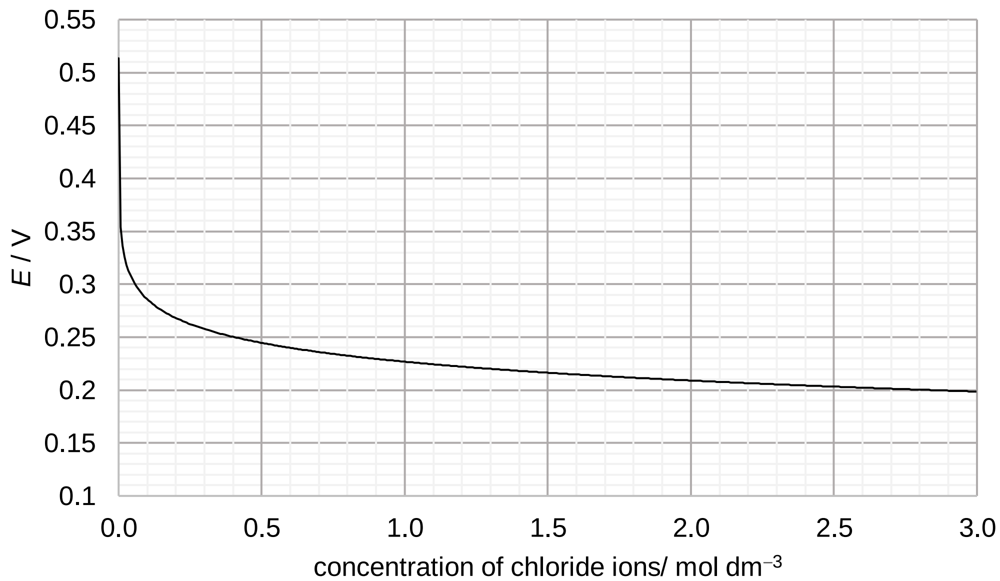
Explain why this is so. [1]

At 298 K, the electrode potential of the silver chloride electrode, *E*, can be estimated from the concentration of silver ions present using formula (1):

$$E = 0.80 - 0.0591 \log \frac{1}{[Ag^+]} \quad \text{.....formula (1)}$$

(ii) Using the expression given, calculate the value of *E* in each of the following cases:
- in pure water and
- when the addition of sodium chloride results in a chloride ion concentration of 2.5 mol dm^{-3}. [3]

(iii) Using the graph given below, suggest why sodium chloride solution ranging from 1.0 mol dm^{-3} to 3.0 mol dm^{-3} is typically used in the setting up of a silver chloride electrode rather than pure water.



[1]

(iv) A student attempted to study the validity of formula (1) by adding aqueous ammonia to vary the concentration of silver ions in solution. This is due to the ability of ammonia to form a complex with the silver ions, thus decreasing its concentration in solution.

Explain a potential problem that may arise with this method of analysis. [1]

(v) The silver chloride electrode is used in many medical equipment. In a particular device used for electrocardiography, a layer of silver metal with a thickness of 1mm is plated onto an electrode with a surface area of 0.12 cm^2 before coating it with solid silver chloride.

If a current of 15.0 mA is used for the electroplating process, calculate the time required to completely plate the silver metal onto the electrode from a solution containing $Ag^+(aq)$.

[The density of silver metal is 10.5 g cm^{-3}]

[2]

(c) When sodium halides react with concentrated sulfuric acid, an acid-base reaction takes place resulting in the formation of white fumes of hydrogen halides.

$$Na\mathbf{X}(s) + H_2SO_4(l) \longrightarrow H\mathbf{X}(g) + NaHSO_4(s), \text{ where } \mathbf{X} = Cl, Br \text{ or } I$$

Subsequently, depending on the reducing strength of the hydrogen halides, a further reaction might take place with concentrated sulfuric acid, resulting in the formation of halogens, a sulfur-containing product and water.

The observations for the reaction of the different sodium halides with concentrated sulfuric acid are shown below:

sodium halide	observations
Na*Cl*	white fumes of HC*l*
NaBr	white fumes of HBr red-brown Br_2 gas which condenses to form a red-brown liquid colourless and pungent SO_2 gas
NaI	white fumes of HI violet I_2 gas which condenses to form a black solid colourless and pungent H_2S gas

(i) Write a balanced molecular equation for each of the following reactions:

- between gaseous HBr and concentrated H_2SO_4
- between gaseous HI and concentrated H_2SO_4 [2]

(ii) Arrange the hydrogen halides in order of increasing reducing strength. Explain your answer, using relevant information from the *Data Booklet* to support the difference in observations. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When a 1.00 g sample of sulfur was dissolved in 1 dm^3 of an organic solvent, the following equilibrium was established:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

The percentages by mass of S_7 and S_8 at equilibrium are:

ring size	S_7	S_8
percentage by mass	0.76	98.92

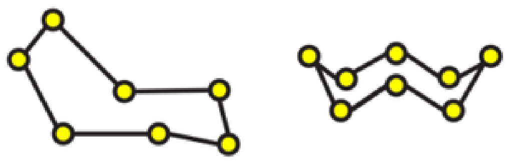
(a) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium. [2]

(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

(iii) The amount of S_8 is increased by 0.01 mol at time t_1. Sketch, on the same axes, two graphs to show how $[S_7]$ and $[S_8]$ vary from t_1 to t_2, the time when equilibrium is re-established at the same temperature.
[You are only required to label the concentrations at t_1.] [2]

(iv) An inert gas is then added at constant pressure. State and explain how the position of equilibrium would change. [2]

The shape of the S_7 and S_8 molecules are as follows.



S_7 S_8

(b) **(i)** Define the term bond energy with reference to the S–S bonds in S_8. [1]

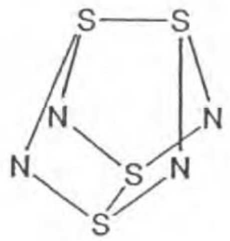
(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction between S_7 and S_8. [1]

(iii) Using your answers in **(a)(ii)** and **(b)(ii)**, and given that:

$$\Delta G^{\ominus} = -RT \ln K_c$$

where T is in Kelvins and ΔG is in J mol^{-1}, calculate the standard entropy change of the reaction. [2]

(c) Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4. In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The four nitrogen atoms are arranged in a plane, with two sulfur atoms above the plane, and two sulfur atoms below the plane. The shape of a molecule of S_4N_4 is as shown.



S_4N_4

Using the data provided below, construct an energy cycle to calculate the average S–N bond energy in S_4N_4.

enthalpy change of formation of S_4N_4	+460 kJ mol^{-1}
enthalpy change of atomisation of sulfur	+297 kJ mol^{-1}
enthalpy change of atomisation of nitrogen	+497 kJ mol^{-1}
S–S bond energy in S_4N_4	+204 kJ mol^{-1}

[3]

(d) Sulfur and tungsten has certain similarities since both atoms have a total of six valence electrons, even though sulfur is a main group element and tungsten is a transition metal. Both elements reach their maximum +6 oxidation state when combined with electronegative elements such as fluorine and oxygen.

(i) Sulfur trioxide, SO_3 and tungsten(VI) oxide, WO_3 differ markedly in their physical properties. While SO_3 is a gaseous pollutant used in industrial preparation of sulfuric acid, WO_3 is used in electrochromic windows, allowing the windows to change colour when an electrical voltage is applied. Their boiling points are 44.9 ^{o}C and 1700 ^{o}C respectively.

With reference to the structure and type of bonding, account for the difference in boiling points. [3]

(ii) Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}.

Draw the structure of WO_4^{2-}. State the shape and bond angle of the O–W–O bond. [2]

[Total: 20]

5 **(a)** The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

N_2H_4 has a boiling point of 114 ^{o}C and decomposes to its elements when passed over a suitable catalyst. The rapid production of hot gaseous products is what provides the thrust.

(i) With the aid of a balanced equation, define the term standard enthalpy change of formation for hydrazine. [2]

(ii) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_r^{\ominus} = -241.0 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change for the decomposition of 1 mol of hydrazine to its elements using data below.

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
NH_3	–46.1
H_2O_2	–187.8
H_2O	–285.8

[2]

(b) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as 'C-Stoff', and hydrogen peroxide ('T-Stoff'). The standard enthalpy change of combustion of hydrazine and methanol are −622.2 kJ mol^{-1} and −726.0 kJ mol^{-1}.

The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol. The densities of hydrazine and methanol are 1.021 g cm^{-3} and 0.7918 g cm^{-3} respectively.

Calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel, assuming that all the hydrazine and methanol are fully combusted.

[2]

(c) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, that is, the reactants ignite spontaneously on contact.

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4. Briefly explain why. [2]

(ii) Draw the structure of N_2O_4, indicating clearly the shape and bond angle around each nitrogen atom. [2]

(iii) At room temperature, N_2O_4 exists as a gas while N_2H_4 is a liquid. With reference to their structure and bonding, account for this difference. [3]

(d) At 46 ^oC, N_2O_4 (colourless gas) exists in equilibrium with nitrogen dioxide, NO_2 (brown gas) with an equilibrium constant, K_p of 0.66 atm. The equation for the equilibrium is

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(i) Write an expression for the equilibrium constant, K_p. [1]

(ii) A certain amount of N_2O_4 is allowed to dissociate in a vessel. At equilibrium, the partial pressure of NO_2 is found to be 0.332 atm.

Calculate the partial pressure of N_2O_4 and total pressure at equilibrium. [2]

(iii) Hence, determine the percent dissociation of N_2O_4 at 46 ^oC. [2]

(iv) State and explain what may be observed when the vessel containing the gases is expanded. [2]

[Total: 20]