Section A

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

1 **(a)** The *dissolved oxygen concentration* (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below 5 mg dm^{-3}, most species of fish cannot survive. [1 g = 1000 mg]

Environmental chemists can determine the DOC in water using the procedure below:

Step 1: A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali. The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.

$$O_2(aq) + 4Mn^{2+}(aq) + 8OH^{-}(aq) + 2H_2O(l) \rightarrow 4Mn(OH)_3(s)$$

Step 2: The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine.

$$2Mn(OH)_3(s) + 2I^{-}(aq) \rightarrow I_2(aq) + 2Mn(OH)_2(s) + 2OH^{-}(aq)$$

Step 3: The iodine formed is then determined by titration with aqueous sodium thiosulfate, $Na_2S_2O_3$(aq).

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$$

25.0 cm^3 of a sample of river water was analysed using the above procedure. The titration requires 24.60 cm^3 of 0.00100 mol dm^{-3} $Na_2S_2O_3$(aq).

(i) Calculate the amount of oxygen present in the 25.0 cm^3 sample of river water.

[2]

(ii) Hence, calculate the dissolved oxygen concentration (DOC), in mg dm^{-3}, in the river water.

[1]

(iii) Comment on whether there is enough oxygen for fish to survive in that river.

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…………………………………………………………………………………………...

[1]

(b) The presence of nitrite ions, NO_2^-, in the river water interferes with this method because NO_2^- ions can also react with iodide ions. During the reaction, NO_2^- is reduced to NO while iodide is oxidised to iodine.

(i) Construct the half–equation for the reduction of NO_2^- to NO in an alkaline medium.

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[1]

(ii) Hence, give the overall equation for the reaction between NO_2^- and iodide ions.

…………………………………………………………………………………………...

[1]

(c) **(i)** An oxide of manganese contains 72.0% by mass of manganese. Determine the empirical formula of this oxide.

[2]

(ii) The oxide in **(i)** is actually an equimolar mixture of two oxides. The oxidation state of manganese in one of the oxides is +3.

Deduce the formulae of the two oxides.

…………………………………………………………………………………………...

[1]

(iii) Hence state the full electronic configuration of manganese existing in the lower oxidation state.

…………………………………………………………………………………………...

[1]

[Total: 10]

2 **(a)** **(i)** Explain what is meant by the term *standard enthalpy change of combustion*, using ethene, C_2H_4 as an example. Illustrate your answer with a balanced equation, including state symbols.

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[2]

(ii) When 0.65 g of ethene was burnt under a container with 100 g of water, the temperature of the water rose from 28^{o}C to 86.5^{o}C. The process is known to be 75% efficient.

Use these data and those relevant in the *Data Booklet* to calculate the enthalpy change of combustion of ethene.

[2]

(iii) The heat released when 1 g of a substance is combusted is known as its fuel value (in kJ g^{-1}). Calculate the fuel value of ethene.

[1]

(b) Sorbic acid, a preservative used in cheese has the following structure:

$$\underset{z}{CH_3}\text{-}CH{=}CH\text{-}\underset{y}{CH}{=}\underset{x}{CH}\text{-}CO_2H$$

It is unsaturated like ethene.

(i) State the type of isomerism exhibited by sorbic acid and explain how it arises. Draw the structural formulae of all the possible isomers.

[4]

(ii) State the type of hybridisation found on the carbon atoms labelled **x**, **y** and **z**.

x: ………………………………………………………………..

y: ………………………………………………………………..

z: ………………………………………………………………..

[1]

[Total: 10]

3 Thionyl chloride, SO_2Cl_2, consists of two very important elements from Period 3. It is a liquid at room temperature.

(a) When a sample containing 2 moles of gaseous SO_2Cl_2 is placed in a 2.0 dm^3 vessel, it decomposes to SO_2 and Cl_2 as shown in the equation below.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \qquad \Delta H \text{ negative}$$

At equilibrium, the total concentration of the mixture is determined to be 1.56 mol dm^{-3}.

(i) Calculate the value of K_c, giving its units.

[3]

(ii) Draw the dot-and-cross diagram for SO_2Cl_2 and state the shape of the molecule.

[2]

(iii) Explain how an increase in temperature would change the value of K_c.

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....

....

....

....

[2]

(b) Phosphorus, another Period 3 element, forms a wide range of chlorides. Most famous are PCl_3 and PCl_5.

(i) Explain briefly why PCl_5 is a solid whereas SO_2Cl_2 is a liquid at room temperature.

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[2]

(ii) PCl_5 is an acidic chloride that hydrolyses in water to produce HCl and H_3PO_4. Similarly, SO_2Cl_2 reacts with water to form two strong acids.

Write a chemical equation, with state symbols, to depict the hydrolysis of SO_2Cl_2 in water.

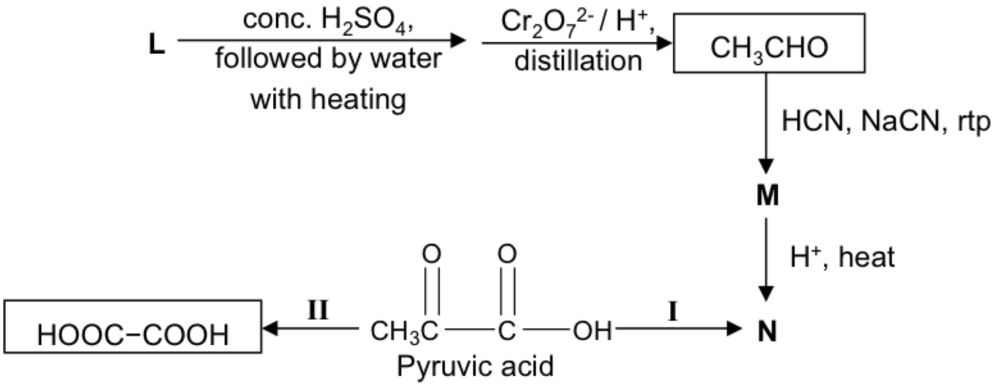
…………………………………………………………………………………………...

[1]

[Total: 10]

4 This question is about the chemistry of some organic compounds.

(a) Pyruvic acid, CH_3COCO_2H, is an important component in living cells as it is involved in the aerobic process of supplying energy. The flow chart shows a series of reactions starting with compound **L**, which has an empirical formula of CH_2.



(i) Draw the structures of compounds **L, M** and **N** in the boxes below.

L	M	N

[3]

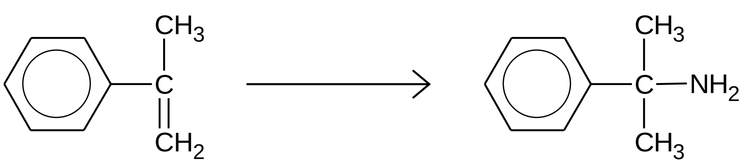
(ii) State the reagents and conditions for steps **I** and **II**.

Step I: ....

Step II: ....

[2]

(b) Compound **F** can be converted to **G** via a series of reactions.

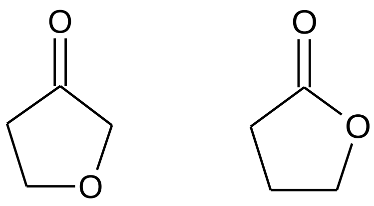


F **G**

Suggest a 2-step synthesis for the conversion of **F** to **G**. State clearly the intermediate, reagents and conditions for each step.

[3]

(c) Suggest a simple chemical test by which the two compounds **X** and **Y** can be distinguished. State the reagents and conditions and the observations expected for each compound.



X **Y**

Reagents and conditions: ……………………………………………………………………….

Observations: ……………………………………………………………………………….

……………………………………………………………………………………………….

……………………………………………………………………………………………….

[2]

[Total: 10]

Section B

Answer **two** questions from this section on separate answer papers.

5 Ocean acidification is the ongoing decrease in the pH of the Earth's oceans caused by the uptake of CO_2 in the atmosphere.

When CO_2 reacts with water, carbonic acid, H_2CO_3 is formed and this causes acidification and affects marine life.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

The following equilibrium is established in ocean water:

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$

HCO_3^- and its conjugate base, CO_3^{2-} are the main components in the ocean that regulates its pH.

It was known that ocean water has become 30% more acidic in terms of H^+ concentration over the last 150 years.

(a) **(i)** A 100 g sample of ocean water saturated with pure carbon dioxide at atmospheric pressure contains 0.165 g of dissolved CO_2.

Assuming that ocean water contains only CO_2 and water with a density of 1 g cm^{-3}, calculate the concentration of dissolved CO_2, in mol dm^{-3}, in the sample.

[2]

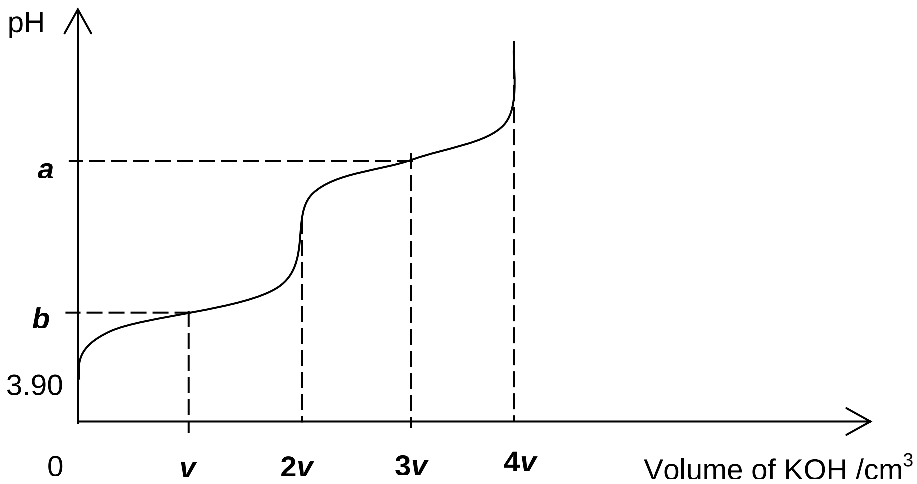
(ii) If the pH of ocean water 150 years ago was 8.25, calculate its current pH.

[2]

(iii) With the aid of equations, explain how the pH of the ocean is regulated.

[2]

(b) A 25.0 cm^3 sample of the same solution in **(a)(i)** is titrated with aqueous KOH and the titration curve is shown below.



H_2CO_3 is a diprotic weak acid and dissociates as shown in the following equations.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad K_{a1}$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_{a2}$$

(i) Write an expression for the first acid dissociation constant, K_{a1}, for H_2CO_3. [1]

(ii) Justify that H_2CO_3 is a weak acid with relevant calculations. [2]

(iii) Express the concentration of KOH used in the titration, in terms of ***v***. [1]

(iv) Suggest, with a reason, a suitable indicator for the first end point of this titration. [1]

(c) Mercury(II) chloride is often used in the testing of samples of ocean water as it can stop biological activity and is therefore able to preserve nutrients in the samples. During the tests, oxalate ions react with mercury(II) chloride in the following reaction.

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2Cl^-(aq) + 2CO_2(g) + 2Hg_2Cl_2(s)$$

The initial rate of this reaction was determined for several concentrations of $HgCl_2$ and $C_2O_4^{2-}$, and the following data were obtained.

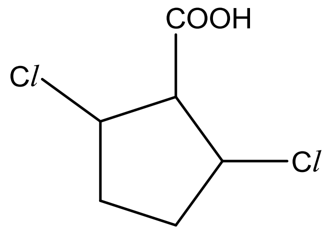
Experiment	Concentration of $HgCl_2$ /mol dm^{-3}	Concentration of $C_2O_4^{2-}$ /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	0.164	0.150	3.2×10^{-5}
2	0.164	0.450	2.9×10^{-4}
3	0.082	0.450	1.4×10^{-4}
4	0.100	0.250	?

(i) Using the data given above, determine the order of reaction with respect to $HgCl_2$ and $C_2O_4^{2-}$. [2]

(ii) Hence, determine the rate equation and calculate a value for the rate constant of the reaction, stating its units. [2]

(iii) Determine the initial rate for Experiment 4. [1]

(d) When samples of ocean water near a plastic manufacturing facility are tested, it was found to contain trace amounts of compound **S**.



Compound **S**

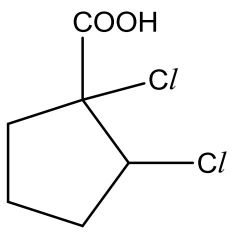
(i) Draw the structures of the organic products (if any) formed when compound **S** reacts with:

(I) hot aqueous NaOH

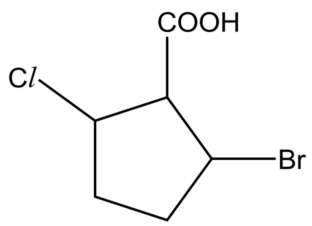
(II) $NaBH_4$ in ethanol

[2]

(ii) Suggest how the acidity of compound **S** may compare with the following compounds **T** and **U**:



Compound **T**



Compound **U**

[2]

[Total: 20]

6 The size of an atom can be measured using the distance between the nuclei of two atoms. For example, the 'metallic radius' of the Na atom is half the distance between two Na atoms in the crystal lattice of the metal. The 'covalent radius' of the C*l* atom is taken to be half the distance between the nuclei in a Cl_2 molecule. Finally, the 'van der Waals' radius' of the Ar atom is assumed to be half the distance between two atoms in the solid state.

These three types of radius are commonly known as 'atomic radii'.

The table below contains the resulting atomic radii for the Period 3 elements.

Element	Na	Mg	A*l*	Si	P	S	C*l*	Ar
atomic radius /nm	0.186	0.160	0.143	0.117	0.110	0.104	0.099	0.192

(a) **(i)** Explain the general trend in atomic radius across Period 3.
[2]

(ii) Suggest a reason for the anomaly in the measurement of atomic radius for Ar.
[1]

(b) **(i)** State the general relationship between atomic radius and first ionisation energy across Period 3.
[1]

(ii) Explain why the relationship does not hold from:

I. Mg to A*l*
II. P to S
[2]

(c) **A**, **B** and **C** are Period 3 elements, from Na to S, inclusive.

- **A** has the highest melting point among Period 3 elements.
- **B** has the highest electrical conductivity in Period 3.
- **C** burns in air with a coloured flame.
- **B** and **C** can show the same oxidation state in their compounds.

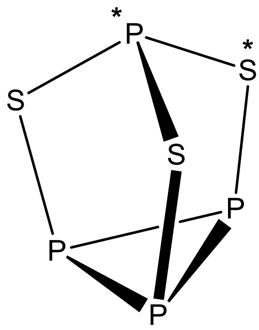
(i) Identify **A**, **B** and **C** and hence give the chemical formulae for their highest oxide.
[1]

(ii) From the three oxides in **(c)(i)**, identify the oxide with

I. the highest melting point;
II. the lowest pH in solution
[1]

(iii) Write equations, including state symbols, to show the acid-base properties of the three oxides in **(c)(i)**.
[4]

(d) Phosphorus sesquisulfide, P_4S_3, is commonly found on the tip of “strike anywhere” matches.



Phosphorus sesquisulfide

(i) By using the VSEPR theory, state the shape and bond angle around the 2 atoms marked with an asterisk (*).

[2]

When a match is struck on a rough surface, the heat generated by friction ignites P_4S_3 in the presence of an oxidising agent. This causes rapid combustion to take place according to the following equation.

$$P_4S_3(s) + 8O_2(g) \xrightarrow{\Delta H_{rxn} = -3676 \text{ kJ mol}^{-1}} P_4O_{10}(s) + 3SO_2(g)$$

(ii) Use the values below to calculate a value for the enthalpy change of formation of $P_4S_3(s)$.

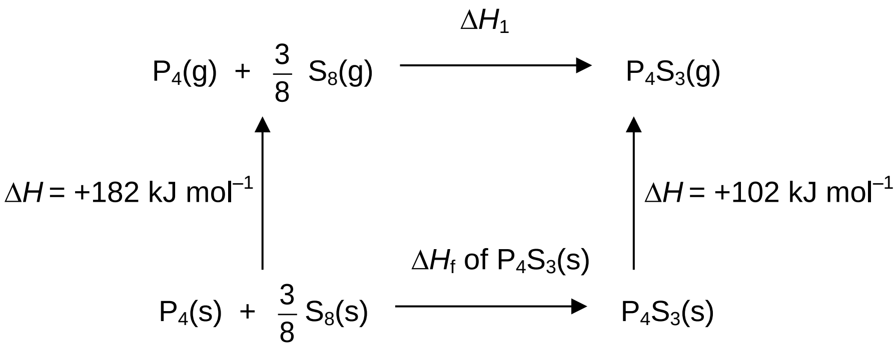
Compound	ΔH_f (kJ mol^{-1})
$P_4O_{10}(s)$	–2940
$KCl(s)$	–436
$SO_2(g)$	–297

[2]

(iii) Define the term ‘*bond energy*’.

[1]

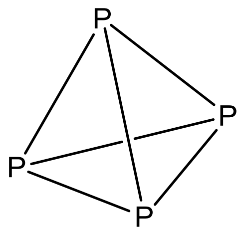
(iv) Using the energy cycle below, and the value calculated in **(d)(ii)**, determine the value for ΔH_1.



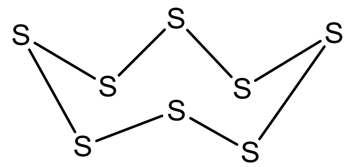
[1]

(v) Hence, with reference to the diagram for P_4S_3 and that of elemental phosphorus and sulfur given below, calculate the bond energy of P–S.

Use any relevant data from the *Data Booklet*, taking bond energy of P–P to be 197 kJ mol^{-1}.



P_4



S_8

[2]

[Total: 20]

7 Both ethanal, CH_3CHO and propanone, CH_3COCH_3 are used extensively in industries as simple precursor molecules for organic synthesis.

(a) Under suitable conditions propanone and ethanal undergo an *aldol* reaction to form **P** of molecular formula $C_5H_{10}O_2$ as one of the products. The following reactions were carried out to determine the structure of **P**.

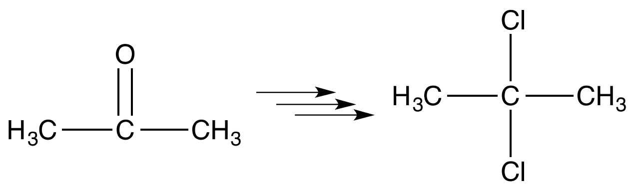
P reacts with 2,4-dinitrophenylhydrazine to give bright orange crystals. Treatment of **P** with alkaline aqueous iodine at 60°C and then addition of dilute acid to the reaction mixture gives pale yellow crystals and a compound **Q** with molecular formula $C_3H_4O_4$.

When **P** is heated at 170°C with excess concentrated sulfuric acid, compound **R** with molecular formula C_5H_8O is formed. **R** can undergo oxidative cleavage with acidified potassium manganate(VII) to give compounds **S**, $C_3H_4O_3$ and **T**, $C_2H_4O_2$.

Deduce the structures of **P, Q, R, S** and **T** and explain the reactions that occurred.

[7]

(b) PCl_5 reacts with carbonyl compounds in a 1 : 1 molar ratio to give gem–dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom. The following shows the conversion of propanone to its corresponding gem-dichloride, 2,2–dichloropropane through a series of reactions:



propanone 2,2–dichloropropane

(i) Suggest the phosphorus-containing by-product of this reaction.

[1]

(ii) Heating 2,2–dichloropropane with ethanolic KOH produces a compound **U**, C_3H_4. Treating **U** with hydrogen over a nickel catalyst produces propane.

Suggest the structure of **U**.

[1]

(iii) Deduce the structure of **V** that gives the following on reaction with PCl_5.

$$\mathbf{V}\ (C_3H_6O_2) \rightarrow CH_2ClCH_2CHCl_2$$

[1]

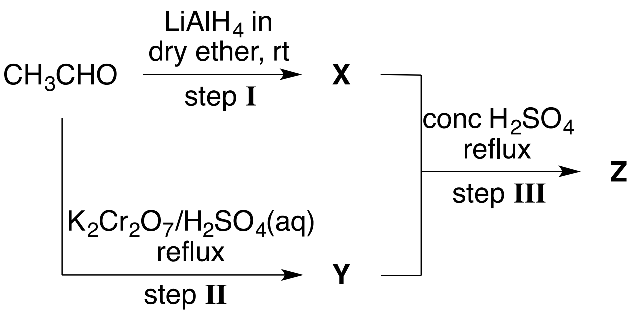
(c) For each of the following reactions, write balanced equations for each step in the reaction scheme. In your equations, give the structures of the organic compounds, **W**, **X**, **Y** and **Z**. You may use [H] and [O] to represent the oxidising and reducing agents respectively.

(i)

$$CH_3CHO \xrightarrow[\text{room temp}]{\text{HCN(aq)/ NaCN(aq)}} \mathbf{W}$$

[1]

(ii)



[3]

(d) The following are data of selected organic compounds.

compound	structure	M_r	boiling point /°C
ethanal	CH_3CHO	44	20.2
propanone	CH_3COCH_3	58	56.0
ethanol	CH_3CH_2OH	46	78.4
trichloromethane	$CHCl_3$	119.5	61.2

Using structure and bonding together with relevant data from above, suggest explanations for the following:

(i) When separate bottles of ethanal and ethanol are opened simultaneously, the smell of ethanal is first detected, followed by ethanol.

[3]

(ii) When equal volumes of propanone and trichloromethane are mixed, there is a rise in temperature. Include a relevant diagram in your answer.

[3]

[Total: 20]