

2015 VJC H1 Chemistry Prelim Exam 8872/2
Suggested Answers

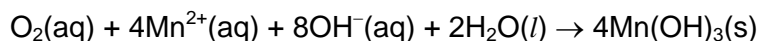
Section A

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

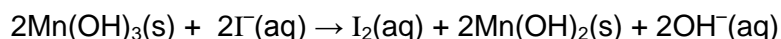
- 1 (a) The *dissolved oxygen concentration* (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below 5 mg dm^{-3} , most species of fish cannot survive.
 [1 g = 1000 mg]

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

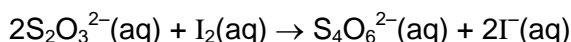
Step 1: A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali. The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+} , forming a pale brown precipitate of $\text{Mn}(\text{OH})_3$.



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



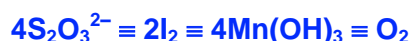
Step 3: The iodine formed is then determined by titration with aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$.



25.0 cm^3 of a sample of river water was analysed using the above procedure. The titration requires 24.60 cm^3 of $0.00100 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$.

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

$$\begin{aligned} \text{Amount of } \text{S}_2\text{O}_3^{2-} \text{ reacted in titration} &= 0.00100 \times \frac{24.60}{1000} \\ &= 2.46 \times 10^{-5} \text{ mol} \end{aligned}$$



$$\begin{aligned} \text{Amount of } \text{O}_2 \text{ present} &= \frac{1}{4} \times 2.46 \times 10^{-5} \\ &= 6.15 \times 10^{-6} \text{ mol} \end{aligned}$$

[2]

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

$$\begin{aligned} \text{DOC} &= 6.15 \times 10^{-6} \times 32.0 \times \frac{1000}{0.025} \\ &= 7.87 \text{ mg dm}^{-3} \end{aligned}$$

[1]

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

Since the actual DOC exceeds 5 mg dm^{-3} , there is enough oxygen for the fish to survive.

[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.



[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.

	Mn	O
Mass %	72.0	$100 - 72.0 = 28.0$
Number of moles of atoms	$72.0 \div 54.9 = 1.311$	$28.0 \div 16.0 = 1.75$
÷ by smaller number	1	1.335
Simplest ratio	$1 \times 3 = 3$	$1.335 \times 3 = 4$

Empirical formula of the oxide is Mn_3O_4 .

[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.

Mn_2O_3 and MnO

[1]

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

Lower oxidation state of Mn is +2.

Electronic configuration of Mn^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

[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.

It is the enthalpy change when 1 mole of ethene is completely burnt in an excess of oxygen under standard conditions at 298K and 1 atm.



[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 $28^\circ C$ to $86.5^\circ C$. 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.

$$\text{Heat evolved, } Q = mc\Delta t = 100 \times 4.18 \times (86.5 - 28) \\ = 24453 \text{ J} = 24.45 \text{ kJ (75\%)}$$

$$\text{Actual heat produced} = 24.45 \times \frac{100}{75} = 32.6 \text{ kJ}$$

$$\text{Amount of ethene used} = \frac{0.65}{28.0} = 0.0232 \text{ mol}$$

$$\Delta H_c \text{ of ethene} = - \frac{32.6}{0.0232} = -1405 \text{ kJ mol}^{-1}$$

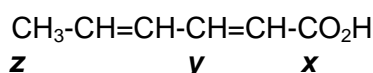
[2]

- (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.

$$\text{Fuel value of ethene} = \frac{1405}{26.0} = 54.0 \text{ kJ g}^{-1}$$

[1]

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

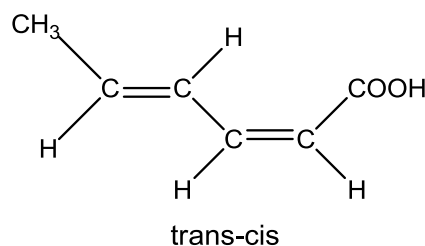
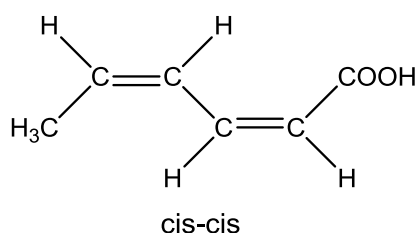


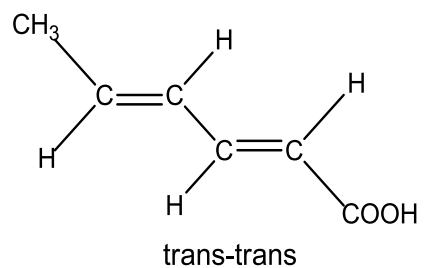
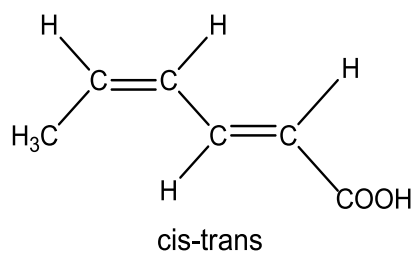
It is unsaturated like ethene.

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

Geometric or cis-trans isomerism arises due to the presence of a C=C bond which prevents free rotation and 2 different groups are across the C=C bond.

Total of 4 isomers are possible since both C=C bonds are able to exhibit cis-trans isomerism.





- (ii) State the type of hybridisation found on the carbon atoms labelled **x**, **y** and **z**. [4]

Both C_x and C_y are sp^2 hybridised

C_z is sp^3 hybridised

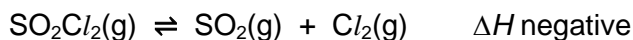
[All 3 correct – 1m ; only 2 correct – 0.5 m]

[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.



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.

$$\text{Initial } [\text{SO}_2\text{Cl}_2] = \frac{2}{2.0} = 1.0 \text{ mol dm}^{-3}$$



initial conc.	$2 / 2.0 = 1$	0	0
change conc.	$-x$	$+x$	$+x$
eqm. conc.	$1 - x$	x	x

$$\begin{aligned} \text{Total concentration at equilibrium} &= (1 - x) + x + x = 1.56 \\ \Rightarrow x &= 0.56 \text{ mol dm}^{-3} \end{aligned}$$

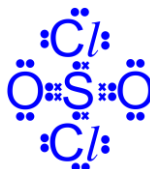
$$[\text{SO}_2\text{Cl}_2]_{\text{eqm}} = 1 - 0.56 = 0.44 \text{ mol dm}^{-3}$$

$$[\text{SO}_2]_{\text{eqm}} = [\text{Cl}_2]_{\text{eqm}} = 0.56 \text{ mol dm}^{-3}$$

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{0.56 \times 0.56}{0.44} = 0.713 \text{ mol dm}^{-3}$$

[3]

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



4 bond pairs, 0 lone pairs therefore tetrahedral.

[2]

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

K_c value would decrease. The reaction is exothermic hence according to Le Chatelier's Principle, an increase in temperature would cause the position of equilibrium to shift left to remove excess heat. This would result in less product form.

[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.

PCl_5 is a non-polar molecule with instantaneous dipole-induced dipole interactions (dispersion forces) whereas SO_2Cl_2 is a polar molecule with permanent dipole-permanent dipole interactions. Since the number of

electrons in PCl_5 is larger, id-id interactions will be stronger than the pd-pd interactions, thus making PCl_5 a solid but SO_2Cl_2 a liquid.

[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.

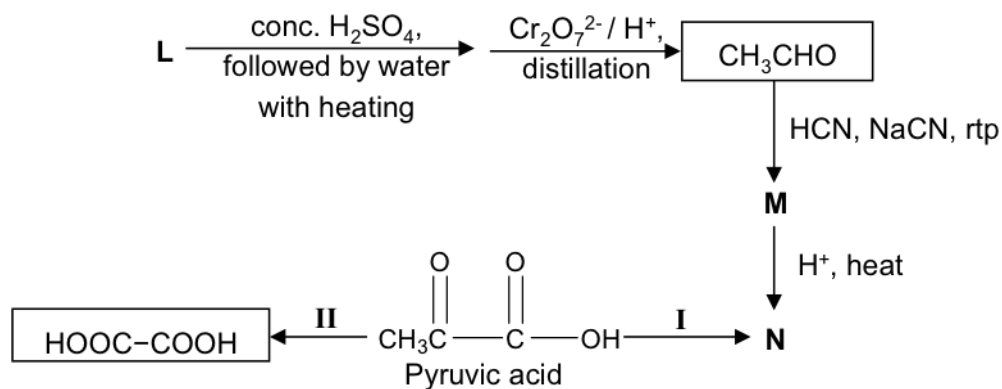


[1]

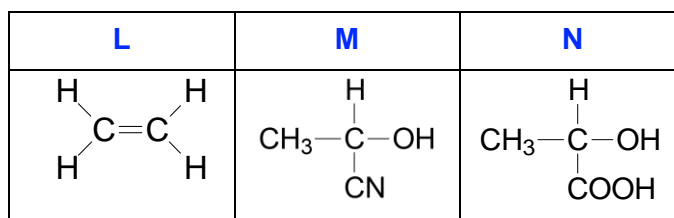
[Total: 10]

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

- (a) Pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, 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.



[3]

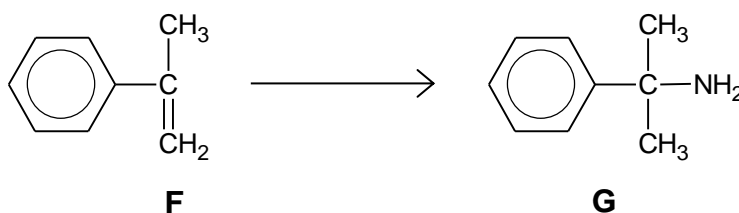
- (ii) State the reagents and conditions for steps **I** and **II**.

Step I: H_2 , Ni (cat), 140°C , OR H_2 , Pt, rtp, OR NaBH_4 in ethanol, rtp

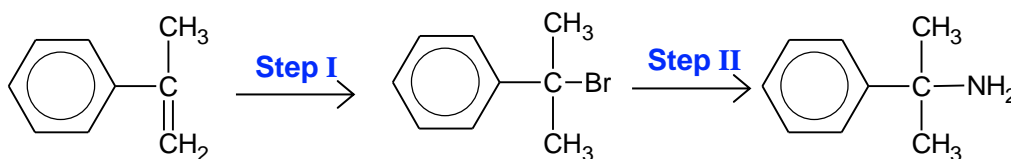
Step II: I_2 (aq), NaOH (aq), warm, followed by H_2SO_4 (aq)
[OR I_2 (aq), NaOH (aq), warm, followed by acidification]

[2]

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



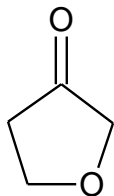
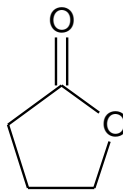
Suggest a 2-step synthesis for the conversion of **F** to **G**. State clearly the intermediate, reagents and conditions for each step.



Step I: HBr , rtp

Step II: Excess $\text{NH}_3(\text{alc})$, heat under pressure in a sealed tube

- (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. [3]

**X****Y**

Test:

Add 2,4-DNPH at rtp to the two unknown in separate test tubes.

Observation:

Orange ppt of hydrazone is formed for the test-tube containing X.

No orange ppt will be formed for the test-tube containing Y.

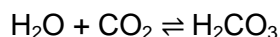
[2]
[Total: 10]

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.



The following equilibrium is established in ocean water:



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.

$$\text{No. of moles of CO}_2 = \frac{0.165}{44.0} = 3.75 \times 10^{-3} \text{ mol}$$

$$\text{Volume of water} = 100 \text{ cm}^3$$

$$\begin{aligned} \text{Concentration of dissolved CO}_2 &= \frac{3.75 \times 10^{-3}}{100} \times 1000 \\ &= 3.75 \times 10^{-2} \text{ mol dm}^{-3} \end{aligned}$$

[2]

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

$$\begin{aligned} \text{pH} &= 8.25 \\ [\text{H}^+] &= 10^{-8.25} \end{aligned}$$

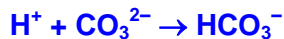
$$\text{Current } [\text{H}^+] \text{ after 150 years} = (130/100) \times 10^{-8.25} = 7.31 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\text{Current pH} = -\lg 7.31 \times 10^{-9} = 8.14$$

[2]

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

When the ocean water becomes slightly more acidic,



A large reservoir of CO_3^{2-} ensures sufficient removal of H^+ to maintain pH.

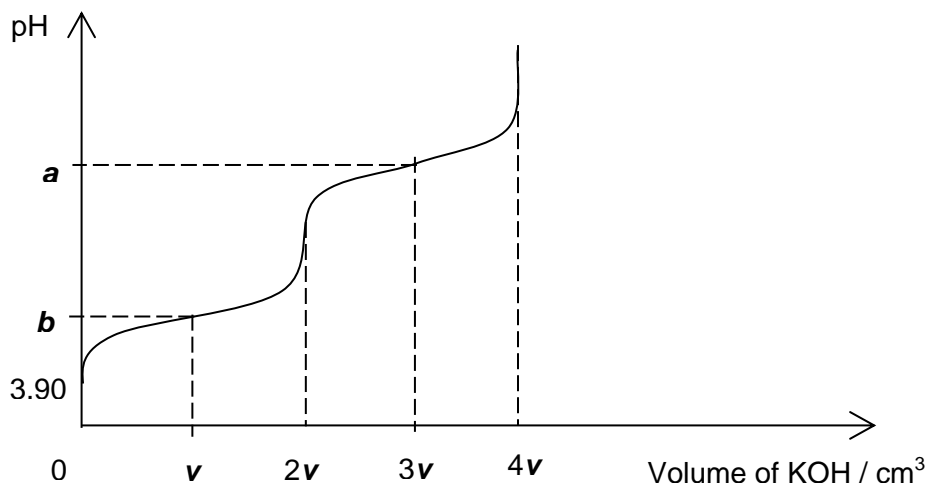
When the ocean water becomes slightly more alkaline,



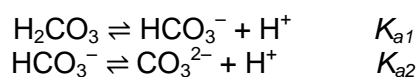
A large reservoir of HCO_3^- ensures sufficient removal of OH^- to maintain pH.

[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.



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

$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

[1]

- (ii) Justify that H_2CO_3 is a weak acid with relevant calculations.

$$\text{Initial } [\text{H}^+] = 10^{-3.90} = 1.26 \times 10^{-4} \text{ mol dm}^{-3} < 3.75 \times 10^{-2} \text{ mol dm}^{-3}$$

H_2CO_3 is partially dissociated in aqueous solution to produce H^+ . Hence, H_2CO_3 is a weak acid.

[2]

- (iii) Express the concentration of KOH used in the titration, in terms of v .

$$[\text{KOH}] = \frac{C_{\text{acid}} \times V_{\text{acid}}}{V_{\text{KOH}}} = \frac{0.0375 \times 25.0}{2v} = \frac{0.47}{v} \text{ mol dm}^{-3}$$

[1]

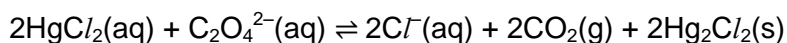
- (iv) Suggest, with a reason, a suitable indicator for the first end point of this titration.

Phenolphthalein / thymol blue

The first equivalence point of a weak acid-strong base titration should be >7 and this lies within the working range of the indicator.

[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.



The initial rate of this reaction was determined for several concentrations of HgCl_2 and $\text{C}_2\text{O}_4^{2-}$, and the following data were obtained.

Experiment	Concentration of HgCl_2 / mol dm^{-3}	Concentration of $\text{C}_2\text{O}_4^{2-}$ / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
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 $\text{C}_2\text{O}_4^{2-}$.

Compare Expt 1 and 2:

When $[\text{C}_2\text{O}_4^{2-}]$ increases by 3 times \Rightarrow rate increases by $\frac{2.9 \times 10^{-4}}{3.2 \times 10^{-5}} = 9 = 3^2$ times.

Hence reaction is second order with respect to $\text{C}_2\text{O}_4^{2-}$.

Compare Expt 2 and 3:

When $[\text{HgCl}_2]$ decreases by 2 times \Rightarrow rate decreases by $\frac{2.9 \times 10^{-4}}{1.4 \times 10^{-4}} = 2$ times.

Hence reaction is first order with respect to HgCl_2 .

[2]

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

$$\text{Rate} = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$$

From Expt 1,

$$k = \frac{3.2 \times 10^{-5}}{0.164 \times 0.150^2} = \underline{8.67 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}}$$

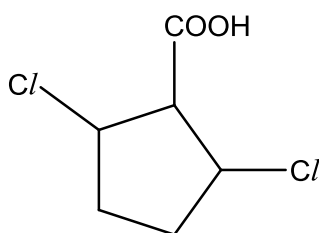
[2]

- (iii) Determine the initial rate for Experiment 4.

$$\begin{aligned} \text{Initial rate} &= 8.67 \times 10^{-3} \times 0.100 \times (0.250)^2 \\ &= \underline{5.42 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

[1]

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

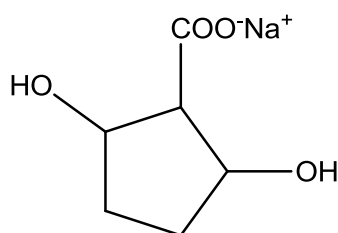
Compound **S**

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

(I) hot aqueous NaOH

(II) NaBH₄ in ethanol

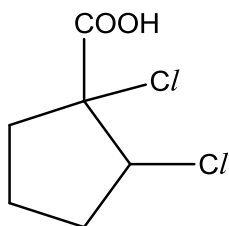
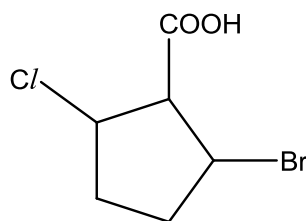
(I) hot NaOH(aq),



(II) NaBH₄, there is no reaction (NaBH₄ can only reduce carbonyl compounds and not carboxylic acids).

[2]

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

Compound **T**Compound **U**

Acidity increases in the order: $U < S < T$

In **S**, in addition to being resonance stabilised, the negative charge on the CH₃COO⁻ anion is further dispersed by the electron-withdrawing inductive effect of the two highly electronegative Cl atoms.

T is more acidic than **S** as the one of the Cl atom is closer to the resonance stabilised CH₃COO⁻ anion and exerts stronger electron-withdrawing inductive effect, thus stabilising the anion.

U is less acidic than **S** as one of the Cl atoms is replaced by a less electronegative Br atom which exerts a weaker electron-withdrawing inductive effect. Hence, the anion of **U** is less stable than the anion of **S**.

[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 Cl atom is taken to be half the distance between the nuclei in a Cl₂ 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	Al	Si	P	S	Cl	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.

Across Period 3, nuclear charge increases as no. of protons increases. Shielding effect remains relatively constant due to the same no. of electron shells. Effective nuclear charge increases. Stronger attraction between nucleus and valence electrons lead to decrease in atomic radius.

[2]

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

The van der Waals' forces holding the two Ar atoms are much weaker than the strong metallic bonds for metals and strong covalent bonds for molecules. Thus, the two atoms for Ar will be further apart leading to a much higher measurement.

[1]

- (b) (i) State the general relationship between atomic radius and first ionisation energy across Period 3.

The first ionisation energy is inversely proportional to atomic radius.

[1]

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

- I. Mg to Al
- II. P to S

From Mg to Al:

It is easier to remove an electron from the 3p orbital of Al compared to the 3s orbital of Mg as it has higher energy and thus less energy is required to removed the electron. [OR it is further away and thus less strongly attracted to the nucleus]. Thus 1st IE decreases from Mg to Al.

From P to S:

It is easier to remove an electron from S due to the inter-electronic repulsion between the paired electrons in the same 3p orbital of S. Thus 1st IE decreases from 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.

A – SiO₂
B – Al₂O₃
C – P₄O₁₀

[1]

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

- I.** the highest melting point;
II. the lowest pH in solution

I. Al₂O₃
II. P₄O₁₀

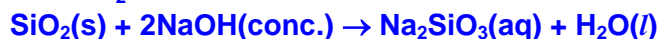
[1]

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

For Al₂O₃:



For SiO₂:

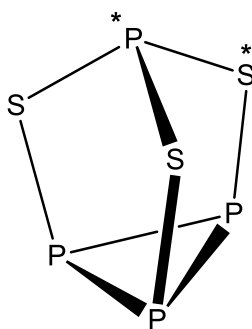


For P₄O₁₀:



[4]

- (d) *Phosphorus sesquisulfide*, P₄S₃, is commonly found on the tip of “strike anywhere” matches.



Phosphorus sesquisulfide

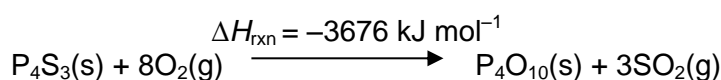
- (i) By using the VSEPR theory, state the shape and bond angle around the 2 atoms marked with an asterisk (*).

Around P: trigonal pyramidal, 107°

Around S: bent or V-shaped, 105°

[2]

When a match is struck on a rough surface, the heat generated by friction ignites P₄S₃ in the presence of an oxidising agent. This causes rapid combustion to take place according to the following equation.



- (ii) Use the values below to calculate a value for the enthalpy change of formation of $\text{P}_4\text{S}_3(\text{s})$.

Compound	ΔH_f (kJ mol^{-1})
$\text{P}_4\text{O}_{10}(\text{s})$	-2940
$\text{KCl}(\text{s})$	-436
$\text{SO}_2(\text{g})$	-297

$$\Delta H_{\text{rxn}} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

$$\Delta H_{\text{rxn}} = \Delta H_f(\text{P}_4\text{O}_{10}) + 3\Delta H_f(\text{SO}_2) - \Delta H_f(\text{P}_4\text{S}_3)$$

$$-3676 = (-2940) + 3(-297) - \Delta H_f(\text{P}_4\text{S}_3)$$

$$\Delta H_f(\text{P}_4\text{S}_3(\text{s})) = -155 \text{ kJ mol}^{-1}$$

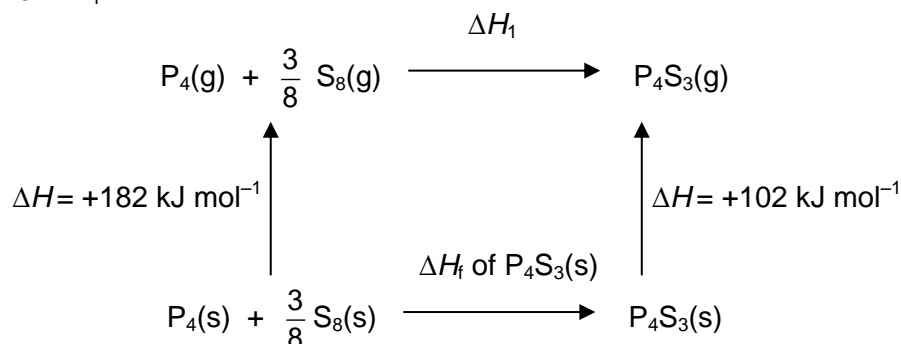
[2]

- (iii) Define the term 'bond energy'.

Bond energy is the energy required to break 1 mole of gaseous covalent bonds in the gaseous state.

[1]

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



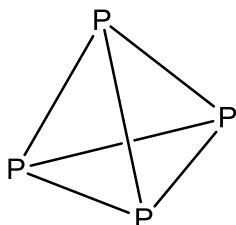
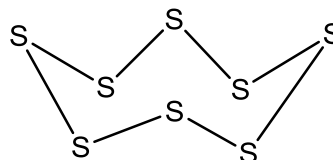
By Hess' Law,

$$\Delta H_1 = -(+182) + (-155) + (+102) = -235 \text{ kJ mol}^{-1}$$

[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

$$\Delta H_{\text{rxn}} = \sum \text{BE}(\text{reactants}) - \sum \Delta H_f(\text{products})$$

$$\Delta H_{\text{rxn}} = 6\text{BE}(\text{P-P}) + 3\text{BE}(\text{S-S}) - 6\text{BE}(\text{P-S}) - 3\text{BE}(\text{P-P})$$

$$-235 = 6(+197) + 3(+264) - 6\text{BE}(\text{P-S}) - 3(+197)$$

$$\text{BE}(\text{P-S}) = 270 \text{ kJ mol}^{-1} \text{ (3 sf)}$$

[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 $\text{C}_5\text{H}_{10}\text{O}_2$ 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 $\text{C}_3\text{H}_4\text{O}_4$.

When **P** is heated at 170°C with excess concentrated sulfuric acid, compound **R** with molecular formula $\text{C}_5\text{H}_8\text{O}$ is formed. **R** can undergo oxidative cleavage with acidified potassium permanganate(VII) to give compounds **S**, $\text{C}_3\text{H}_4\text{O}_3$ and **T**, $\text{C}_2\text{H}_4\text{O}_2$.

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

P undergoes condensation reaction with 2,4-DNPH, giving hydrazones, which appears as bright orange crystals.

⇒ **P** has carbonyl group

P undergoes oxidative cleavage with $\text{I}_2(\text{aq})/\text{OH}^-$, giving CHI_3 , which appears as pale yellow ppt and salt of **Q**.

⇒ **P** contains both $\text{CH}_3\text{CH}(\text{OH})-$ or $\text{CH}_3\text{CO}-$ groups

P reacts with concentrated H_2SO_4

P undergoes elimination/dehydration with conc. H_2SO_4 to give **R**.

⇒ **P** is also an alcohol.

R undergoes oxidative cleavage with KMnO_4/H^+ to give **S** and **T**

⇒ **R** is an alkene/contains $\text{C}=\text{C}$ double bond.

P: $\text{CH}_3\text{COCH}_2\text{CH}(\text{OH})\text{CH}_3$

Q: $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$

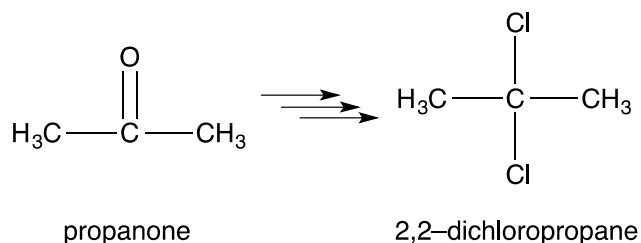
R: $\text{CH}_3\text{COCH}=\text{CH}(\text{CH}_3)$

S: $\text{CH}_3\text{COCO}_2\text{H}$

T: $\text{CH}_3\text{CO}_2\text{H}$

[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:



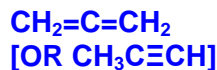
- (i) Suggest the phosphorus-containing by-product of this reaction.

POCl_3

[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**.



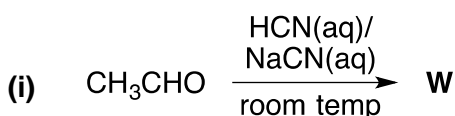
[1]

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

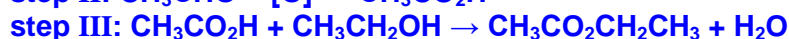
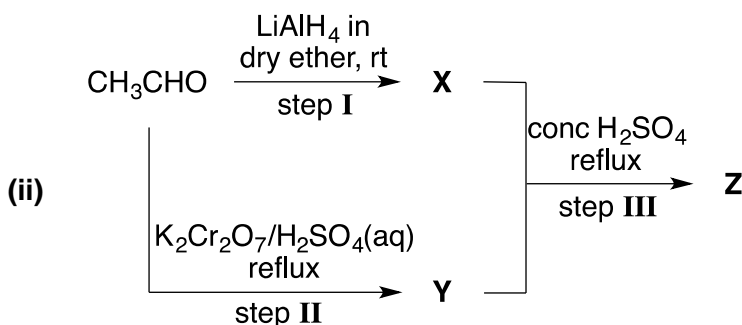


[1]

- (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.



[1]



[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.

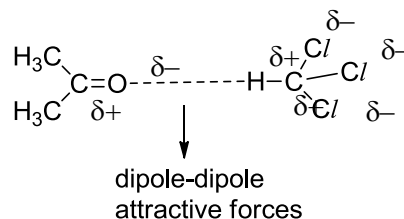
Both are polar with simple molecular structures/ or both are polar simple discrete molecules.

Ethanal molecules are held together by dipole-dipole attractive forces which are weaker than hydrogen bonding between ethanol molecules.

Less amount of energy is required to overcome the forces of attraction between ethanal molecules. Ethanal has a lower boiling point than ethanol and hence ethanal is more volatile.

[3]

- (ii) When 30 cm³ of propanone and 33 cm³ of trichloromethane are mixed at room temperature, there is a rise in temperature. Include a relevant diagram in your answer.



Both are polar with simple molecular structures/ or both are polar simple discrete molecules.

Propanone molecules are held by dipole-dipole interactions. Trichloromethane molecules are also held by dipole-dipole interactions.

When the two compounds are added together compatible dipole-dipole interactions are formed between propanone and trichloromethane molecules, which are strong enough to overcome the original interactive forces of propanone and trichloromethane, hence releasing heat.

[3]

[Total: 20]