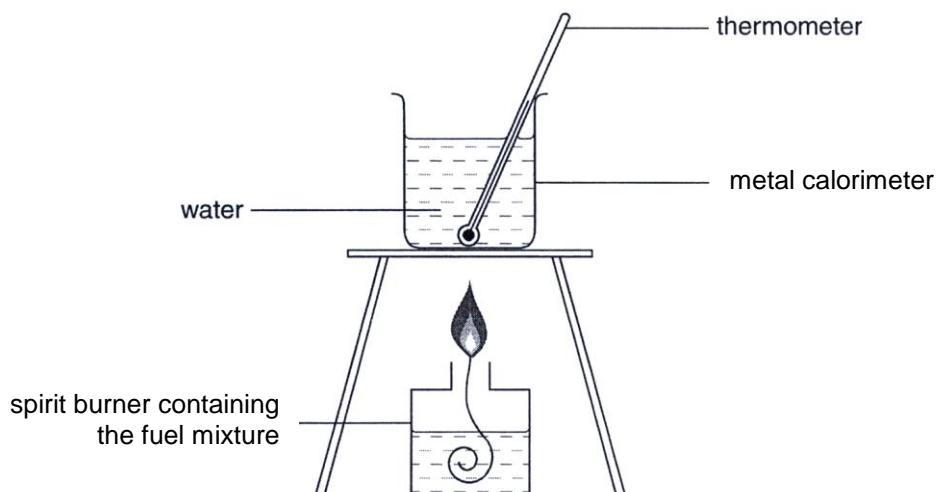


**2014 DHS Year 6 Preliminary Examination**  
**H2 Chemistry 9647/02 Suggested Solutions**

**1 Planning (P)**

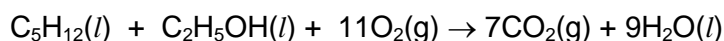
A student was provided with a spirit burner containing a 'fuel mixture' which was prepared by mixing equimolar amounts of pentane and ethanol. The enthalpy change of combustion of this 'fuel mixture' is  $-11.8$  kJ per mole of 'fuel mixture'. He was told to use the enthalpy change of combustion of this 'fuel mixture' to find the heat capacity of a metal calorimeter using the apparatus shown below. Heat capacity is defined as the number of joules of heat needed to raise the temperature of the calorimeter by one Kelvin or one degree Celsius.



Additional information:

1. Specific capacity of water is  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ .
2. The maximum capacity of the metal calorimeter is between  $100$  to  $150 \text{ cm}^3$ .
3. A temperature rise of  $5^\circ \text{C}$  is considered to be significant for this experiment.

- (a) Construct a balanced equation for the complete combustion of the 'fuel mixture' with state symbols. [1]



- (b) Identify one possible source of error and suggest an improvement to overcome this error in the experiment. [2]

Error: Heat loss to the surroundings by the calorimeter and water.

Improvement: Conduct the experiment in a draught-free room.

Also accept: 1. Provide lagging on the metal calorimeter.  
2. Cover the metal calorimeter with a cover/lid.

- (c) Calculate the minimum mass of the fuel mixture required to bring about a  $5^\circ \text{C}$  temperature rise.

Assuming no heat loss,

$$Q = mc\Delta T = (100)(4.2)(5) = 2100 \text{ J}$$

$$\Delta H_c = -2100 / n_{\text{fuel mixture}}$$

$$\Rightarrow -11.8 \times 10^3 = -2100 / n_{\text{fuel mixture}}$$

$$\therefore n_{\text{fuel mixture}} = 2100 / (11.8 \times 10^3) = 0.1779 \text{ mol}$$

$$\Rightarrow \text{minimum mass of fuel mixture} = 0.1779 \times 59.0 = 10.5 \text{ g}$$

[2]

- (d) Write a plan to determine the heat capacity of the metal calorimeter using the apparatus provided.

In your plan you should give details of the procedure (number your steps) and provide a table to record the readings to be taken, including the units. Details about the appropriate mass of water used and temperature rise should also be included.

[4]

- 1) Weigh the spirit burner containing the 'fuel mixture'
- 2) Using a measuring cylinder, measure  $100 \text{ cm}^3$  of water into the metal calorimeter.
- 3) Measure the initial temperature of the water using a thermometer after the water is allowed to stand for a few minutes.
- 4) Light the burner and allow it to heat the water in the calorimeter.
- 5) Monitor the temperature of water using the thermometer, and extinguish the flame when the temperature of the water increases by about  $5^\circ\text{C}$ .
- 6) Measure the highest temperature reached after the flame has been extinguished.
- 7) Cool and reweigh the spirit burner with the remaining 'fuel mixture'.
- 8) Ensure that the mass of the fuel mixture is at least 10.5 g.

Table:

Initial temperature of water/ $^\circ\text{C}$	$T_1$
Final temperature of water/ $^\circ\text{C}$	$T_2$
Initial mass of spirit burner with 'fuel mixture' / g	M
Final mass of spirit burner with remaining 'fuel mixture' /g	N

- (e) Show how you would calculate, from your above proposed plan and experimental results, the heat capacity of the metal calorimeter.

[3]

Since density of water is  $1 \text{ g cm}^{-3}$ , mass of the water in the calorimeter = 100 g

Let the heat capacity of the calorimeter be  $C \text{ J K}^{-1}$

Temperature rise of the water in the calorimeter =  $5^\circ\text{C}$

Heat gained by water and calorimeter  
 $= 100 \times 4.2 \times 5 + C \times 5 = 2100 + 5C \text{ J}$

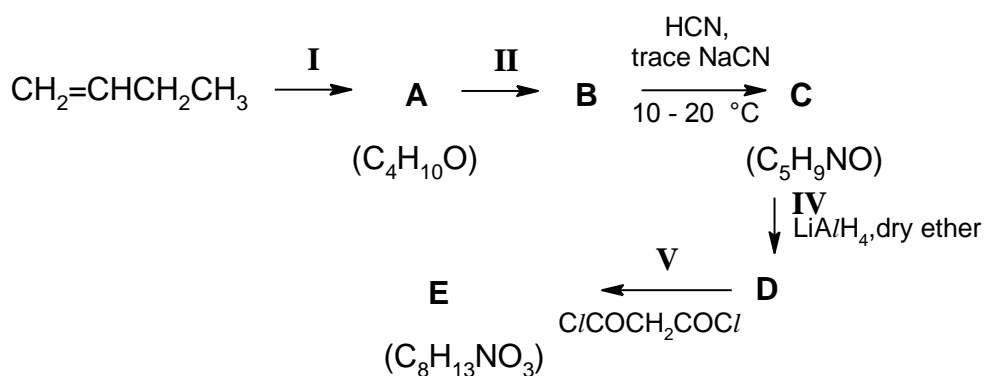
Mass of 'fuel mixture' burned =  $(M-N) \text{ g} = P \text{ g}$   
 Average molar mass of 'fuel mixture' =  $(72 + 46)/2 = 59.0 \text{ g mol}^{-1}$   
 Hence, amount of 'fuel mixture' =  $P/59 \text{ mol}$

Heat lost by 'fuel mixture' =  $11800 \times P/59 = 200P \text{ J}$

Heat lost by 'fuel mixture' = Heat gained by water and calorimeter  
 $200P = 2100 + 5C$   
 $C = 40P - 420$

[Total: 12]

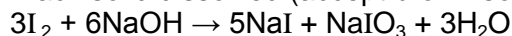
- 2 But-1-ene can be converted to compound E via the following series of reactions.



Both compounds A and B produce a yellow precipitate on warming separately with aqueous alkaline iodine.

- (a) Iodine undergoes a disproportionation reaction with hot dilute NaOH(aq). Describe what is observed and write a balanced equation for the reaction.

Black solid dissolved (accept brown solution) to form a colourless solution.

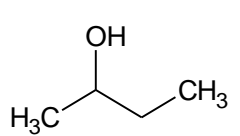
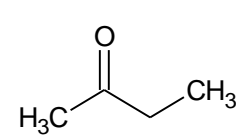
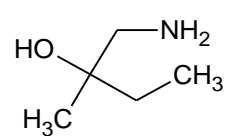
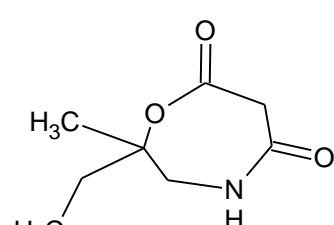


- (b) State the reagents and conditions for steps I and II.

Step I: cold conc  $\text{H}_2\text{SO}_4$  followed by  $\text{H}_2\text{O}$  and heat

Step II: acidified  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ , reflux OR acidified  $\text{KMnO}_4(\text{aq})$ , reflux

- (c) In the boxes below, draw the structural formulae of compounds A, B, D and E.

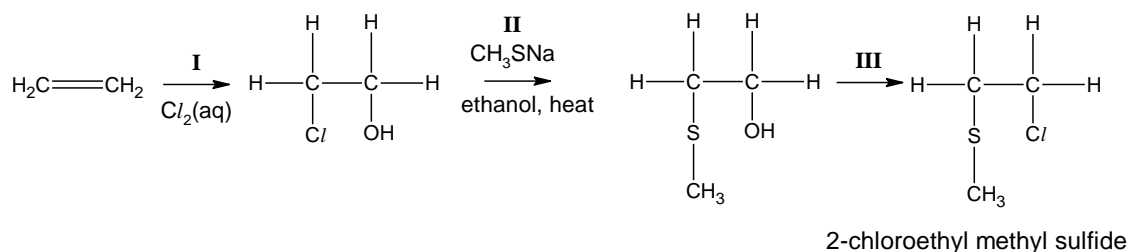
<p>A</p> 	<p>B</p> 
<p>D</p> 	<p>E</p> 

- (d) Explain why the reaction in Step III produces an equimolar mixture of two stereoisomers of compound C.

Compound B is a carbonyl which is planar. The attacking nucleophile can approach the planar carbonyl from the top side or bottom side with equal probability hence resulting in a racemic mixture.

[Total: 9]

- 3 2-chloroethyl methyl sulfide may be synthesised from ethane.



- (a) Describe a simple chemical test to distinguish between  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ , of the reaction in Step III, stating the expected observation for each compound.

Test: Add  $\text{PCl}_5$  to each of the sample.

Observation: White fumes observed for  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ . No white fumes observed for  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ .

- (b) The kinetics of the reaction in Step II was studied.

The experimental results are given in the table below.

Run	$[\text{CH}_3\text{SNa}] / \text{mol dm}^{-3}$	$[\text{CH}_2\text{C}/\text{CH}_2\text{OH}] / \text{mol dm}^{-3}$	Relative rate / $\text{min}^{-1}$
1	0.100	0.150	6
2	0.150	0.150	9
3	0.200	0.200	16

Use the data to determine the order of reaction with respect to both  $\text{CH}_3\text{SNa}$  and  $\text{CH}_2\text{C}/\text{CH}_2\text{OH}$ .

Hence, write a rate equation for the reaction and state the units for the rate constant.

Comparing Run 1 & 2, when  $[\text{CH}_3\text{SNa}]$  increases by 1.5 times and the  $[\text{CH}_2\text{C}/\text{CH}_2\text{OH}]$  remains the same, the relative rate increases by 1.5 times. Hence Order with respect to  $\text{CH}_3\text{SNa}$  is 1.

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{k(0.15)(0.15)^x}{k(0.2)(0.2)^x} = \frac{9}{16} \quad \Rightarrow x = 1$$

Hence Order with respect to  $\text{CH}_2\text{C}/\text{CH}_2\text{OH}$  is 1.

Rate equation:  $\text{Rate} = k[\text{CH}_3\text{SNa}][\text{CH}_2\text{C}/\text{CH}_2\text{OH}]$

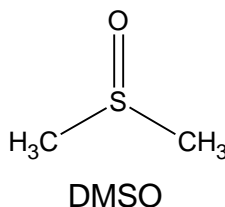
Units for rate constant =  $\text{mol}^{-1} \text{dm}^3 \text{min}^{-1}$

- (c) In organic syntheses, the choice of solvent can affect the rate of a reaction. Ethanol is the solvent of choice in Step II above.

The process of forming ion-dipole interactions between ions and solvent

molecules is called solvation. Polar protic solvents such as ethanol, contains at least one hydrogen atom directly bonded to an electronegative atom. These solvents solvate both cations and anions. It is known that the concentration of ions is inversely proportional to the degree of solvation of the ions involved.

Polar aprotic solvents contain no hydrogen atom directly bonded to an electronegative atom. These solvents solvate cations well, but not anions. Dimethyl sulfoxide (DMSO) is an example of a polar aprotic solvent.



- (i) State the ion which acts as the nucleophile in the reaction in Step II.

Nucleophile:  $\text{CH}_3\text{S}^-$

- (ii) Suggest why DMSO does not solvate anions effectively.

The partial positive charge formed on the sulfur atom of DMSO does not form effective ion-dipole interactions with anions due to the presence of two methyl groups that provide some steric effect. The two electron-donating methyl groups may decrease the partial positive charge on the sulfur atom. DMSO lacks hydrogen atoms which are capable of forming hydrogen bonding with anions.

- (iii) With reference to your answers in (b) and (c)(ii), explain why the rate of reaction is 1000 times faster when the reaction in Step II is carried out in DMSO instead of ethanol.

The reaction in Step II is bimolecular and rate is dependent on the concentration of  $\text{CH}_3\text{S}^-$ . The concentration of  $\text{CH}_3\text{S}^-$  will be in greater excess since DMSO will only solvate the cation as compared to ethanol which can solvate both cations and anions. The unsolvated  $\text{CH}_3\text{S}^-$  will therefore be more available to attack the electrophile  $\text{CH}_2\text{C}/\text{CH}_2\text{OH}$ .

- (d) Sodium methanethiolate, used in Step II,  $\text{CH}_3\text{SNa}$ , can be made from methanethiol,  $\text{CH}_3\text{SH}$ .

Although methanethiol is structurally similar to methanol, the two compounds have significant different  $\text{p}K_{\text{a}}$  values at 298 K.

compound	formula	$\text{p}K_{\text{a}}$
methanol	$\text{CH}_3\text{OH}$	15.5
methanethiol	$\text{CH}_3\text{SH}$	10.4

Explain briefly why methanethiol has a smaller  $\text{p}K_{\text{a}}$  value than methanol.

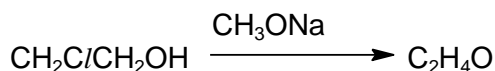
Methanethiol is more acidic than methanol as methanol is considered neutral.

The resultant anion produced by methanethiol  $\text{CH}_3\text{S}^-$  is more stable than that of  $\text{CH}_3\text{O}^-$ . Sulfur is a larger atom than oxygen atom and therefore, the electron density cloud on the sulfur atom is more diffused than that of oxygen atom.

OR

Methanethiol is more acidic than methanol as methanol is considered neutral. The S–H bond is a longer and weaker bond compared to the O–H bond. Hence, methanethiol has a greater tendency to release a  $\text{H}^+$ .

- (e)  $\text{CH}_2\text{Cl}/\text{CH}_2\text{OH}$  reacts with  $\text{CH}_3\text{ONa}$  to give compound W,  $\text{C}_2\text{H}_4\text{O}$ .



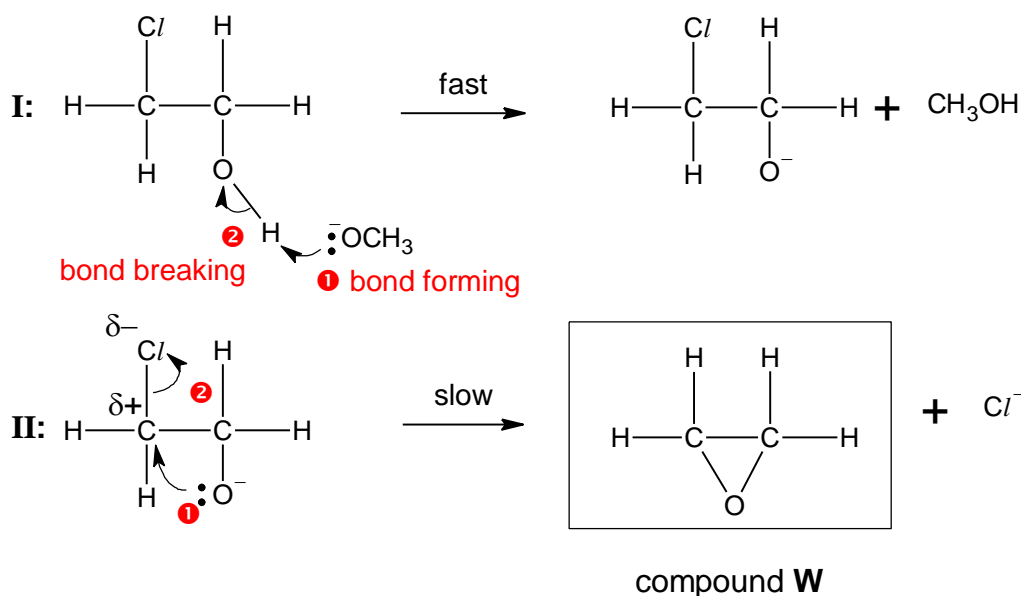
The reaction between  $\text{CH}_3\text{ONa}$  and  $\text{CH}_2\text{Cl}/\text{CH}_2\text{OH}$  occurs in two steps.

The first step involves an acid-base reaction.

The second step involves an intramolecular reaction and it is rate determining.

In each step below,

- label the partial charges and lone pair of electrons on the reacting species,  $\text{CH}_2\text{Cl}/\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{Cl}/\text{CH}_2\text{O}^-$ .
- draw curly arrows to show the flow of electrons during the reaction.
- draw the displayed formula of compound W.

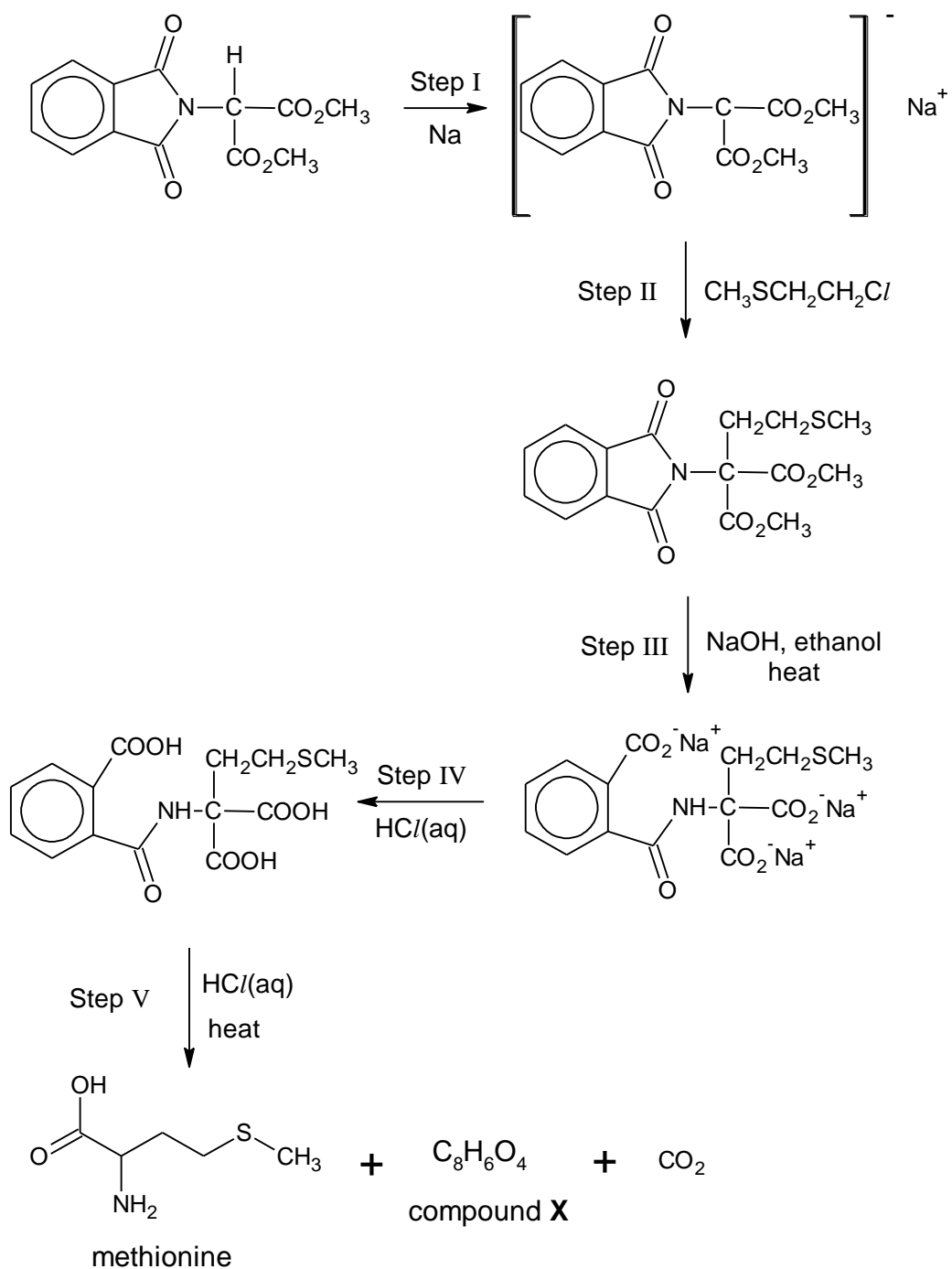


[Total: 15]

- 4 Sulfur compounds can be used in the synthesis of organic compounds. Methionine is an  $\alpha$ -amino acid which is essential to humans and is also used by plants to synthesise ethane.

- (a) In the 1930s, Barger and Weichselbaum reported the synthesis of methionine

using the sodium salt of ethyl phthalimidomalonate and 2-chloroethyl methyl sulfide.



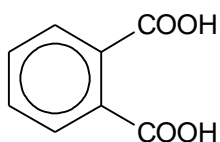
- (i) What type of reaction are steps I and III?

Step I: neutralisation

Step III: (basic) hydrolysis

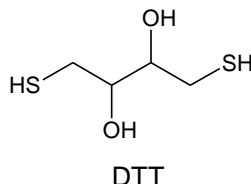
- (ii) Compound X,  $\text{C}_8\text{H}_6\text{O}_4$ , obtained as a by-product in Step V, is sparingly soluble in water. 1 mol of X reacts with exactly 1 mol of sodium carbonate.

Give the structure of compound X.



[3]

- (b) Dithiothreitol (DTT) is used in biochemical laboratories to maintain *tertiary* proteins. The structure of DTT is shown below.



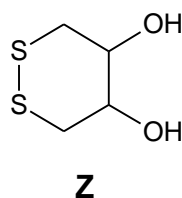
- (i) Suggest two suitable R group interactions between DTT and an amino acid side chain of a tertiary protein.

Disulfide bridges, hydrogen bonding, ion-dipole interactions.

- (ii) Predict the number of optical isomers for DTT which results in optical activity and explain why DTT has this number of optical isomers.

DTT has 3 optical isomers. DTT has 2 chiral centres which should give rise to a maximum of 4 optical isomers. However, DTT is a symmetrical molecule such that 2 of the optical isomers are the same. Hence, DTT has only 3 optical isomers.

- (iii) DTT can be used to form Z.



Suggest the type of reaction for the conversion of DTT to Z and state the type of stereoisomerism exhibited by Z. Name a natural  $\alpha$ -amino acid that is able to undergo such a reaction.

Type of reaction: oxidation

Type of stereoisomerism: geometric isomerism

Amino acid: cysteine

[6]

[Total: 9]

- 5 Phosphorus is able to form various compounds with halogens such as chlorine. An example of a compound formed between phosphorus and chlorine is phosphorus trichloride. At 373 K, both phosphorus trichloride and chlorine exist as gases.

- (a) State one assumption in the kinetic theory of gases that causes the deviation of a



real gas from ideal behaviour.

[1]

Any one of the following assumptions:

- The volume occupied by the molecules is negligible relative to the volume of the container.
- The forces of attraction between molecules (intermolecular attraction) as well as between the molecules and walls of the container are negligible.
- Gases are made up of molecules which are in constant random motion in straight lines.
- Pressure is due to collisions between the molecules and the walls of the container.
- All collisions, both between the molecules themselves, and between the molecules and the walls of the container, are perfectly elastic. (That means that there is no loss of kinetic energy during the collision.)
- The temperature of the gas is proportional to the average kinetic energy of the molecules.

(b) Predict with reasons, which of the two gases will deviate more from ideality.

[2]

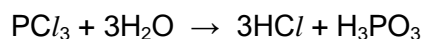
- Both  $\text{PCl}_3$  ( $M_r = 137.5$ ) and  $\text{Cl}_2$  ( $M_r = 71.0$ ) are simple molecular substances.
- However  $\text{PCl}_3$  has a larger number of electrons OR a larger electron cloud. This allows larger and stronger dipoles to be set up between  $\text{PCl}_3$  molecules. Stronger temporary dipole-dipole interactions exist between  $\text{PCl}_3$  molecules.
- In addition, permanent dipole-dipole interactions also exist between polar  $\text{PCl}_3$  molecules.
- Strength of van der Waals forces of attraction is stronger between  $\text{PCl}_3$  molecules.
- Thus  $\text{PCl}_3$  deviates more from ideality.

OR

- $\text{PCl}_3$  ( $M_r = 137.5$ ) is a larger molecule than  $\text{Cl}_2$  ( $M_r = 71.0$ ).
- The volume occupied by  $\text{PCl}_3$  molecules is larger and more significant relative to the volume of the container than that of  $\text{Cl}_2$  molecules.
- Thus  $\text{PCl}_3$  deviates more from ideality.

(c) Phosphorus trichloride can react with water to form 2 compounds, a phosphorus based compound and a non-phosphorus based compound.

- (i) Write a balanced equation for the reaction between phosphorus trichloride and water.

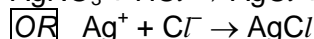
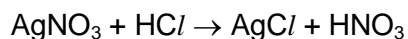


Note: State symbols, whether correct or wrong, were ignored.

- (ii) Describe what happens when aqueous silver nitrate is added to aqueous solution of the non-phosphorus based compound. Write balanced equation(s) for the reaction, if any.

[2]

White precipitate of AgCl formed.



Note: State symbols, whether correct or wrong, were ignored.

- (d) Phosphorus triiodide is frequently used in organic synthesis and can be prepared by addition of iodine to phosphorus in carbon disulfide. Alternatively, phosphorus triiodide can be formed by reacting phosphorus trichloride with hydrogen iodide.

- (i) Write a balanced equation for the preparation of phosphorus triiodide.

Any one of the following equations:

- $\text{P}_4 + 6\text{I}_2 \rightarrow 4\text{PI}_3$
- $2\text{P} + 3\text{I}_2 \rightarrow 2\text{PI}_3$   $\boxed{\text{OR}} \quad \text{P} + \frac{3}{2}\text{I}_2 \rightarrow \text{PI}_3$
- $\text{PCl}_3 + 3\text{HI} \rightarrow \text{PI}_3 + 3\text{HCl}$

Note: State symbols, whether correct or wrong, were ignored.

- (ii) State the physical state and colour of iodine under room conditions.

Black Solid

Note:

- Colours 'brown' and 'purple' were *not* accepted.
- $\frac{1}{2}$  marks were *not* awarded to answers that were partially correct.

- (iii) Write the electronic configuration of iodine-131 using the noble gas core configuration and state the number of protons and neutrons in iodine-131.

Electronic configuration:  $[\text{Kr}] 4d^{10} 5s^2 5p^5$

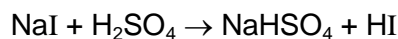
Number of protons = 53 (atomic number from *Data Booklet*)

Number of neutrons =  $131 - 53 = 78$

- (iv) Explain, with the aid of balanced equations, why low yield of hydrogen iodide will be obtained when concentrated sulfuric acid is reacted with solid sodium iodide.

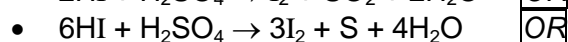
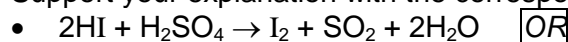
[7]

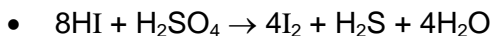
[Total: 12]



- The hydrogen iodide produced in the initial reaction is strongly reducing.
- It further reduces concentrated sulfuric acid to  $\text{SO}_2$   $\boxed{\text{OR}} \text{S}$   $\boxed{\text{OR}} \text{H}_2\text{S}$ , while itself is oxidised to iodine.
- Thus low yield of hydrogen iodide is obtained.

Support your explanation with the corresponding equation:





Note: State symbols, whether correct or wrong, were ignored.

6 This question is about periodic trends that can be observed in the Periodic Table and thermal stability of Group II elements. The thermal decomposition of Group II carbonates can be investigated by heating the respective carbonates and recording the total volume of carbon dioxide evolved.

- (a) (i) Write an equation to represent the thermal decomposition of calcium carbonate.



- (ii) How and why does the magnitude of the lattice energy of calcium carbonate differ from its residue after it has been formed from decomposition?

$$\text{L.E} \propto \frac{q_+ q_-}{r_+ + r_-}$$

Both  $\text{CO}_3^{2-}$  and  $\text{O}^{2-}$  anions are doubly charged.

But  $\text{CO}_3^{2-}$  has a larger ionic radius/size than  $\text{O}^{2-}$  anion.

Thus, magnitude of the lattice energy of  $\text{CaCO}_3$  is smaller than that of  $\text{CaO}$ .

- (iii) Given that the decomposition of  $\text{MgCO}_3$  is an endothermic process, predict and explain the sign of  $\Delta G$  for the reaction at high temperatures.

$\Delta S$  is positive ( $> 0$ ) due to

Increase in no. of moles of gas in the products

$$\Delta G = \Delta H - T\Delta S$$

$$|T\Delta S| > |\Delta H|$$

$\Delta G$  becomes negative ( $< 0$ ) at high temperatures.

- (iv) A 4.19 g sample of a carbonate of a Group II metal, X, lost 1.25 g in mass when heated strongly. Identify metal X.



$$\text{Amount of CO}_2 = 1.25/44.0 = 0.0284 \text{ mol}$$

$$\text{Amount of XCO}_3 = 0.0284 = 4.19/M_r \text{ of XCO}_3$$

$$M_r \text{ of XCO}_3 = 147.5$$

$$147.5 = A_r \text{ of X} + 12.0 + 3(16.0)$$

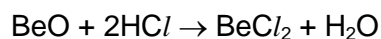
$$A_r \text{ of X} = 87.5$$

X is strontium.

[8]

- (b) Beryllium, in Period 2, is the only element in Group II that shares very similar chemical properties with aluminium which is in Period 3.

- (i) Write the balanced equation for the reaction of  $\text{BeO}$  with dilute  $\text{HCl}(\text{aq})$ .



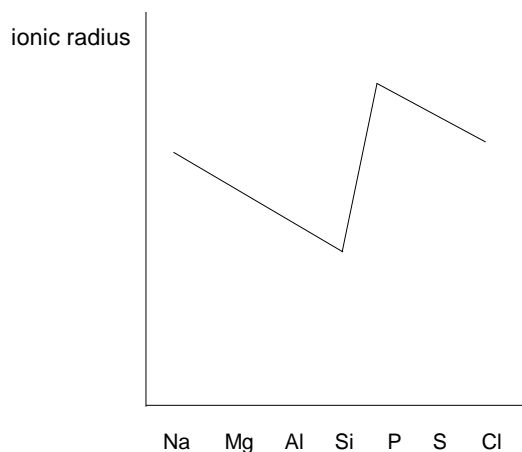
- (ii) Describe what happens if dilute  $\text{NaOH(aq)}$  is slowly added to the solution in (i) until in excess.

A white precipitate formed.

The precipitate dissolves to form a colourless solution.

[3]

- (c) (i) Sketch the ionic radius of the elements in Period 3 on the axes provided.



- (ii) Explain the shape of the sketch.

There are two isoelectronic series in period 3.

Within each series, an increasing number of protons or nuclear charge and constant screening effect (same no of electrons) results in increasingly stronger nuclear attraction experienced by the valence electrons or increasing effective nuclear charge.

Valence electrons are pulled closer to nucleus, leading to a decreasing trend in ionic radius.

Anionic series has a larger size than cationic series as the valence electrons are in a higher principal quantum shell or have 1 more filled shell. Hence, experience weaker nuclear attraction and are less tightly held.

[4]

[Total: 15]