



Chemistry Paper 2 Suggested Solutions with Marker's comments

- 1 Mount Ijen in East Java is famous for its rare blue flames, visible at night. The phenomenon occurs when sulfur vapour, from the volcano's cracks burns, producing bright blue flames and sulfur dioxide. In the cool high-altitude air, some of the vapour condenses into solid sulfur.

- (a) A team of environmental chemists were authorised to collect solid sulfur deposits near Mount Ijen's crater to investigate volcanic activity.

The chemists burnt the sulfur sample and measured the temperature change for a fixed amount of water placed in a calorimeter. The data from their experiment is shown in Table 1.1.

**Table 1.1**

mass of solid sulfur powder burnt /g	0.76
mass of water in beaker /g	150
initial temperature of water /°C	29.8
final temperature of water /°C	39.7

- (i) Construct an equation to represent the standard enthalpy change of combustion of solid sulfur, S.

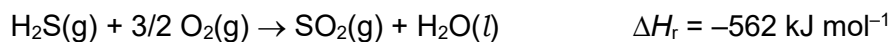


- (ii) Calculate the enthalpy change of combustion of solid sulfur, S, based on their experiment.

$$\begin{array}{lcl}
 q = -mc\Delta T & & \Delta H = \frac{q}{n} = \frac{-6207.3}{\frac{0.76}{32.1}} \\
 = -150 \times 4.18 \times (39.7 - 29.8) & & = -262176 \text{ J mol}^{-1} \\
 = -6207.3 \text{ J} & & = -262 \text{ kJ mol}^{-1}
 \end{array}$$

[2]

- (iii) During volcanic activity, many sulfur-containing gases such as hydrogen sulfide,  $\text{H}_2\text{S}$ , and sulfur dioxide,  $\text{SO}_2$ , are released. In the atmosphere,  $\text{H}_2\text{S}$  can oxidise to form  $\text{SO}_2$ , and subsequently sulfur trioxide,  $\text{SO}_3$ , may be formed.



Use the data given in Table 1.2 to calculate the enthalpy change of combustion of solid sulfur, S.

**Table 1.2**

compound	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{H}_2\text{S}(\text{g})$	-20.6
$\text{H}_2\text{O}(\text{l})$	-285.8

$\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$  represents  $\Delta H_f(\text{SO}_2)$  and also represents  $\Delta H_c(\text{S})$

$$\begin{aligned} \Delta H_r &= [\Delta H_f(\text{SO}_2) + (-285.8)] - (-20.6) \\ -562 &= [\Delta H_f(\text{SO}_2) + (-285.8)] - (-20.6) \\ \Delta H_f(\text{SO}_2) &= -296.8 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta H_f(\text{SO}_2) = \Delta H_c(\text{SO}_2) = \underline{\underline{-297 \text{ kJ mol}^{-1}}}$$

[2]

- (iv) Comment on the difference in values for the enthalpy change of combustion of solid sulfur determined in (a)(ii) and (a)(iii).

For (a)(ii), the heat lost to the surroundings was not accounted for / the experiment was not 100% efficient / the sulfur sample from the volcano was not pure. [1]

- (v) With reference to a relevant chemical equation, explain how the release of sulfur-containing gases during volcanic activity can have a negative impact on the environment.



$\text{SO}_3$  dissolves in water to result in the formation of acid rain that can lead to soil degradation/destruction of crops and farmlands / corrosion of buildings or structures / water acidification that harms marine life. [2]

- (b) Sulfur in volcanic emissions primarily exists as a mixture of two stable isotopes:  $^{32}\text{S}$  and  $^{34}\text{S}$ .

The chemists analysed volcanic gas samples to determine the isotopes' relative abundance, which reveals the sulfur's origin.

- If the sample was enriched in  $^{32}\text{S}$ , it originated from deep mantle degassing.
- If the sample was enriched in  $^{34}\text{S}$ , it originated from hydrothermally recycled sources.

- (i) 1.994 g of  $\text{SO}_2$  evolved at Mount Ijen allowed the chemists to extract 1.00 g of elemental sulfur containing mixture of isotopes,  $^{32}\text{S}$  and  $^{34}\text{S}$ , for further analysis.

Calculate the percentage by mass of  $^{32}\text{S}$  in the elemental sulfur extracted. You may use the chemical formula S to represent elemental sulfur in your calculations.

Let the mass of  $^{32}\text{S}$  to be  $x$  g and  $^{34}\text{S}$  to be  $(1.00 - x)$  g.

$$\text{amount of } ^{32}\text{S} = \frac{x}{32} \text{ mol}$$

$$\text{amount of } ^{34}\text{S} = \frac{1.00 - x}{34} \text{ mol}$$

$$\begin{aligned} \text{Molar mass of } ^{32}\text{SO}_2 &= 32 + (16 \times 2) \\ &= 64 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{Molar mass of } ^{34}\text{SO}_2 &= 34 + (16 \times 2) \\ &= 66 \text{ g/mol} \end{aligned}$$

$$\text{S} \equiv \text{SO}_2$$

$$\left( \frac{x}{32} \times 64 \right) + \left( \frac{1.00 - x}{34} \times 66 \right) = 1.994$$

$$2x + 1.941 - 1.941x = 1.994$$

$$0.059x = 0.053$$

$$x = 0.898$$

$$\begin{aligned} \text{\% by mass of } ^{32}\text{S} &= \frac{0.898}{1.00} \times 100\% \\ &= 89.8\% \end{aligned}$$

alternatively

$$\begin{aligned} \text{amount of O} &= \frac{1.994 - 1.00}{16} \\ &= 0.062125 \text{ mol} \end{aligned}$$

$$\text{S} \equiv 2\text{O}$$

$$\frac{x}{32} + \frac{1.00 - x}{34} = \frac{0.062125}{2}$$

$$x = 0.898$$

[3]

- (ii) Hence, suggest the likely origin of the sulfur sample.

Deep mantle degassing, since \% by mass of  $^{32}\text{S}$  is significantly higher/ the sample is enriched in  $^{32}\text{S}$ . [1]

While volcanic emissions affect the isotopic fractions of sulfur, the natural isotopic abundance of sulfur in Earth's environment is generally found to be present as follows.

**Table 1.3**

isotope	relative isotopic mass	percentage abundance / %
$^{32}\text{S}$	31.972	95.02
$^{33}\text{S}$	32.971	0.75
$^{34}\text{S}$	33.968	4.21
$^{36}\text{S}$	35.967	0.02

- (iii) Use the data in Table 1.3 to calculate the relative atomic mass of sulfur, giving your answer to two decimal places.

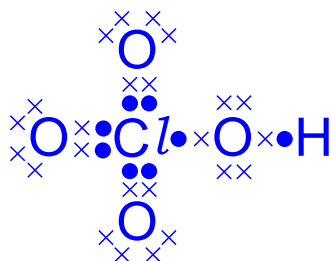
$$\begin{aligned}
 A_r \text{ of sulfur} &= \frac{95.02 \times 31.975 + 0.75 \times 32.971 + 4.21 \times 33.968 + 0.02 \times 35.967}{100} \\
 &= 32.06 \text{ (2 d.p.)}
 \end{aligned}$$

[1]

[Total: 13]

- 2 Group 17 elements form a range of oxoacids with different oxidation states, such as  $\text{HClO}_4$ .

- (a) (i)  $\text{HClO}_4$  has two central atoms; one chlorine atom and one oxygen atom. In addition, the H atom is bonded to a O atom. Draw the dot-and-cross diagram of  $\text{HClO}_4$ .



[1]

- (ii) Use VSEPR to describe and explain the shape and bond angle about central Cl and O atom in  $\text{HClO}_4$ .

About both O and Cl atoms have 4 electron pairs. To minimise repulsion, the electrons pairs are directed as far apart as possible, to corners of tetrahedron.

About O, there are 2 bond pairs and 2 lone pairs and it is bent shape while about

Cl there are 4 bond pairs and it has tetrahedral shape.

Extent of repulsion: lone pair-lone pair > lone pair-bond pair > bond pair-bond pair. Hence bond angle about O and Cl is 104.5° and 109.5° respectively. [3]

- (b) With reference to your answer in (a)(i), explain why  $\text{HFO}_4$  does not exist?  
 Fluorine does not have energetically available and accessible d orbitals for expansion of octet.  
 Or F is too small to accommodate 4 oxygen atoms around it  
 Or F is too electronegative to donate its electron pair for dative bonding [1]

- (c) The Latimer diagram of some chlorine species in acidic solution is given in Fig. 2.1.

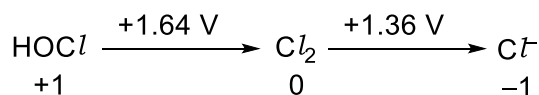
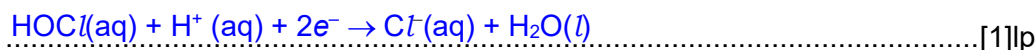


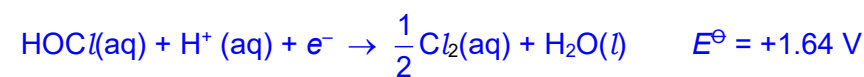
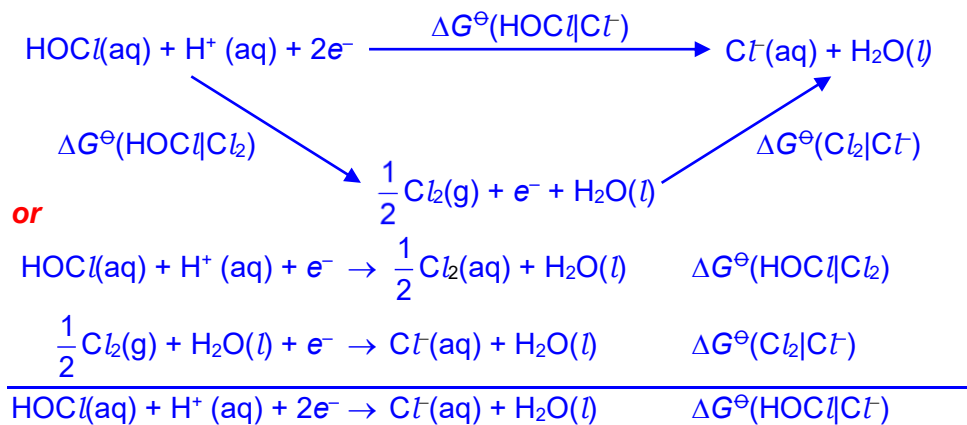
Fig 2.1

In Latimer diagram, oxidation numbers decrease from left to right and the numerical values of  $E^\ominus$  of two adjacent species in volts. For example, the diagram shows that  $E^\ominus(\text{HOCl}|\text{Cl}_2)$  is +1.64 V.

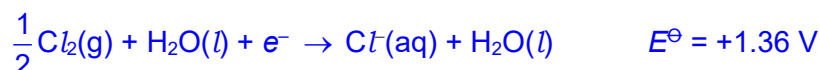
- (i) Write a half-equation for the conversion of one mole of  $\text{HOCl}$  to one mole of  $\text{Cl}^-$  in acidic solution at 298 K.



- (ii) Hess' Law is applicable to  $\Delta G^\ominus$  in the same manner as  $\Delta H^\ominus$ .  
With reference to the *Data Booklet* and Fig. 2.1, calculate  $\Delta G^\ominus$  for the conversion of one mole  $\text{HOCl}$  to one mole of  $\text{Cl}^-$  in acidic solution.



$$\Delta G^\ominus(\text{HOCl}|\text{Cl}_2) = -nFE^\ominus = -1 \times F \times (+1.64) = -1.64F \text{ J mol}^{-1}$$



$$\Delta G^\ominus(\text{Cl}_2|\text{Cl}^-) = -nFE^\ominus = -1 \times F \times (+1.36) = -1.36F \text{ J mol}^{-1}$$

$$\begin{aligned} \Delta G^\ominus(\text{HOCl}|\text{Cl}^-) &= \Delta G^\ominus(\text{HOCl}|\text{Cl}_2) + \Delta G^\ominus(\text{Cl}_2|\text{Cl}^-) \\ &= -1.64F - 1.36F = -3.00F \\ &= -289500 \\ &= -290 \text{ kJ mol}^{-1} \end{aligned}$$

[3]

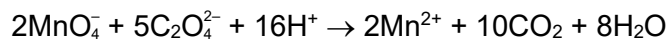
- (iii) Hence, calculate the standard electrode potential for the  $\text{HOCl}|\text{Cl}^-$  half-cell.

$$E^\ominus(\text{HOCl}|\text{Cl}^-) = \frac{\Delta G^\ominus(\text{HOCl}|\text{Cl}^-)}{-nF} = \frac{-3.00F}{-2F} = +1.50 \text{ V}$$

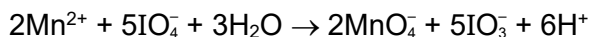
[1]

- (d) A sample of group 2 metal ethanedioate,  $\text{MC}_2\text{O}_4$ , is analysed to determine the identity of the metal.

A 4.13 g sample of the metal ethanedioate is reacted with excess acidified potassium manganate(VII),  $\text{KMnO}_4$ .

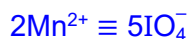


A  $25\text{ cm}^3$  portion from the remaining solution is reacted with periodate ions,  $\text{IO}_4^-$ , to produce  $\text{IO}_3^-$  and  $\text{MnO}_4^-$ .  $22.2\text{ cm}^3$  of  $0.2\text{ mol dm}^{-3}$  of  $\text{IO}_4^-$  was required to react with the manganese(II) ions.



Deduce the identity of the metal in the metal ethanedioate.

$$\text{amt of } \text{IO}_4^- = 0.2 \times 0.0222 = 0.00444\text{ mol}$$



$$\text{amt of } \text{Mn}^{2+} \text{ in } 25\text{ cm}^3 = 2/5 \times 0.00444 = 0.001776\text{ mol}$$

$$\text{total amt of } \text{Mn}^{2+} \text{ in } 100\text{ cm}^3 = 0.001776 \times 100/25 = 0.007104\text{ mol}$$



$$\text{Hence, amt of } \text{C}_2\text{O}_4^{2-} = 5/2 \times 0.007104 = 0.01776\text{ mol}$$

$$\text{molar mass of } \text{MC}_2\text{O}_4 = 4.13 / 0.01776 \approx 232.5\text{ g/mol}$$

$$A_r \text{ of M} = 232.5 - [(2 \times 12.0) + (4 \times 16.0)] = 144.5$$

The group 2 metal is **barium**.

[3]

- (e) Periodic acid,  $\text{HIO}_4$ , is used as a selective oxidant in organic chemistry to split alcohols with two adjacent hydroxy groups into two carbonyl compounds. An example is shown in Fig. 2.2.

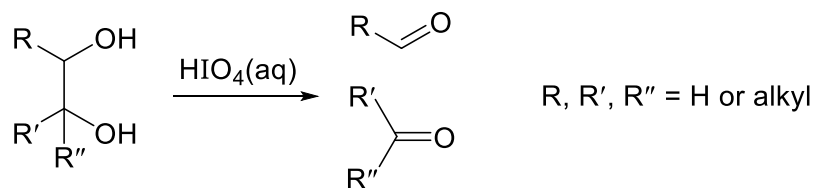


Fig. 2.2

Periodic acid also oxidises hydroxycarbonyl and dicarbonyl compounds by a hydration equilibrium, in which the carbonyl group is first converted into a diol.



For example:

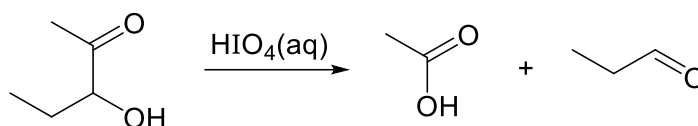


Fig. 2.3

Predict the organic products of the reactions shown in Fig. 2.4.

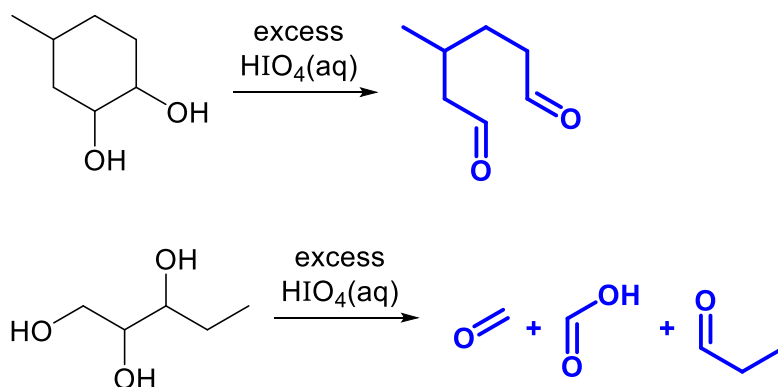


Fig. 2.4

[3]

[Total: 16]



- 3 (a) State whether trichloroethanoic acid or ethanoic acid, is the stronger acid. Explain your answer.

Trichloroethanoic acid is the stronger acid. The more stable the conjugate base, the stronger the acid. Trichloroethanoic acid has 3 Cl substituents which are electron-withdrawing, which helps to disperse the negative charge on the carboxylate group, stabilising the conjugate base. Ethanoic acid has an electron-donating alkyl substituent, which intensifies the negative charge on the carboxylate group, destabilising the conjugate base. [2]

- (b) Phenyl ethanoate is often used as a solvent and as the building block for the synthesis of other chemicals.

- (i) One method of its production involves phenol with an appropriate acid chloride via a **two**-step process. Identify the reactant required for each step.

step 1: NaOH(aq), room temperature

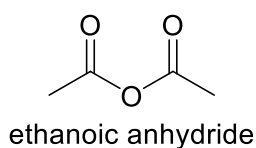
step 2: ethanoyl chloride, CH<sub>3</sub>COCl, room temperature

[2]

- (ii) Give two reasons why phenol does **not** react with carboxylic acids to form esters.

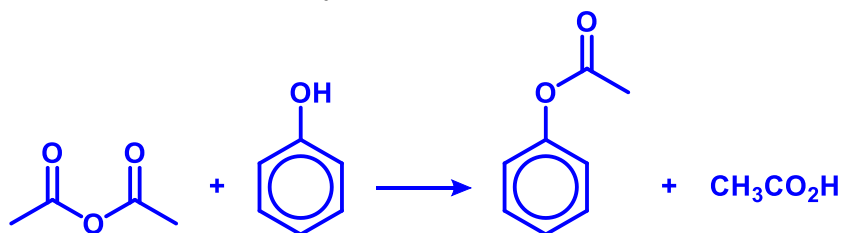
The lone pair of electrons on the oxygen of phenol is delocalised into the benzene ring, rendering phenol to be a weak nucleophile. The lone pair of electrons on oxygen in carboxylic acid delocalised into the C=O bond, rendering the acid to be a weak electrophile, hence there is no reaction. [2]

Another method of production involves phenols reacting with a class of compounds known as acid anhydrides. Ethanoic anhydride, (CH<sub>3</sub>CO)<sub>2</sub>O, is an example of a common commercially available acid anhydride.



Acid anhydrides undergo similar reactions to acid chlorides, and are easier and safer to handle in organic synthesis.

- (c) (i) Write a balanced chemical equation for the formation of phenyl ethanoate using phenol and ethanoic anhydride.



[1]

- (ii) Suggest why acid anhydrides are generally less reactive than acid chlorides towards nucleophiles.

The lone pair of electrons on the C–O–C oxygen of acid anhydrides is more

effectively delocalised into the C=O than that on the Cl of acid chlorides as it

is held in a 2p orbital while the lone pair in Cl is held in a 3p orbital. Hence, the

[1]

acyl carbon is less electrophilic/reactive.

- (d) **R** is formed when an acid anhydride **S**, C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>, reacts with CH<sub>3</sub>NH<sub>2</sub>.

**R** is a neutral compound and has the molecular formula C<sub>8</sub>H<sub>9</sub>NO. **R** reacts with hot H<sub>2</sub>SO<sub>4</sub>(aq) to produce **P** and CH<sub>3</sub>NH<sub>2</sub>.

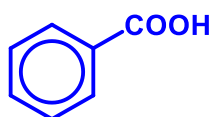
**P** is not very soluble in water, but dissolves after reacting with an excess of Na<sub>2</sub>CO<sub>3</sub>(aq).

- (i) Name the type of reaction occurring when **R** reacts with hot aqueous sulfuric acid.

Hydrolysis or nucleophilic (acyl) substitution. [1]

- (ii) **P** has the molecular formula C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>. **P** can be formed when methylbenzene reacts with acidified potassium manganate(VII).

Draw the structure of **P**.

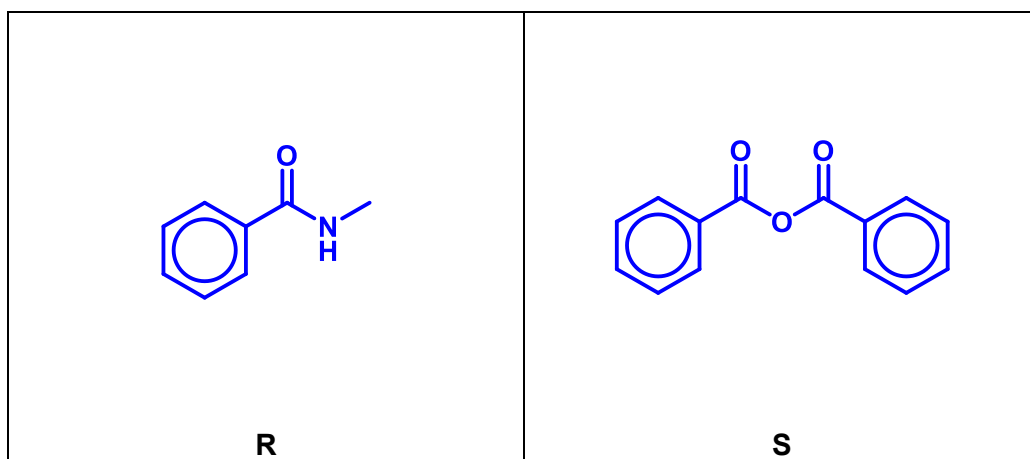


[1]

- (iii) Write the equation for the reaction of **P** with an excess of Na<sub>2</sub>CO<sub>3</sub>(aq).

2C<sub>6</sub>H<sub>5</sub>COOH + Na<sub>2</sub>CO<sub>3</sub> → 2C<sub>6</sub>H<sub>5</sub>COONa + CO<sub>2</sub> + H<sub>2</sub>O [1]

(iv) Suggest the structures of **R** and **S**.



[2]

(v) Use of the *Data Booklet* is relevant to this question.

Infra-red absorptions are useful in identifying functional groups present in molecules.

Suggest an absorption frequency range which can be used to distinguish between molecule **R** and **P**.

3300-3500 (N-H bond) or 1210-1440 (C-O in COOH)  $\text{cm}^{-1}$  ..... [1]

[Total:14]

- 4 Industrial wastewater is wastewater produced by industrial facilities during manufacturing or other processes. It differs from domestic wastewater due to the presence of a wider range of pollutants and the potential for higher concentrations of contaminants.

(a) An industrial facility discharges wastewater containing  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  ions. To meet environmental standards, the facility designs a treatment process by controlled precipitation to remove these ions from the wastewater.

- (i) Table 4.1 shows the  $K_{\text{sp}}$  values for the hydroxides of the metal ions. Given that the wastewater initially contains  $0.010 \text{ mol dm}^{-3}$  of each metal ion, calculate the minimum pH at which copper(II) hydroxide begin to precipitate.

**Table 4.1**

metal hydroxide	$K_{\text{sp}}$	minimum pH for precipitation
$\text{Al}(\text{OH})_3$	$1.3 \times 10^{-33}$	3.70
$\text{Cu}(\text{OH})_2$	$2.2 \times 10^{-20}$	—
$\text{Zn}(\text{OH})_2$	$3.0 \times 10^{-17}$	6.74

Let the concentration of  $\text{OH}^-$  be  $x \text{ mol dm}^{-3}$

$$\begin{aligned}
 K_{\text{sp}} &= (\text{Cu}^{2+})(\text{OH}^-)^2 \\
 2.2 \times 10^{-20} &= 0.01x^2 \\
 x &= 1.483 \times 10^{-9} \\
 \text{pH} &= 14 - \text{pOH} \\
 &= 14 - (-\lg(1.483 \times 10^{-9})) \\
 &= 5.17
 \end{aligned}$$

[2]

- (ii) Based on your calculations in (a)(i), explain how  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the wastewater can be separated in the treatment process.

As each metal hydroxide precipitates at different pH, by gradually increasing the pH of the solution, sequential and selective precipitation of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  ions can occur. [1]

- (b) Industrial wastewater containing  $\text{Cu}^{2+}$  ions must be treated before it can be safe for discharge to a sanitary sewer for further treatment. The allowable limit of  $\text{Cu}^{2+}$  in the discharge is 1 mg per litre.

- (i) Calculate the concentration of  $\text{Cu}^{2+}$  ions in the wastewater when zinc(II) hydroxide starts to precipitate.

When  $\text{Zn}(\text{OH})_2$  starts to precipitate,  
 $\text{pH} = 6.74$ ,  $[\text{OH}^-] = 5.495 \times 10^{-8} \text{ mol dm}^{-3}$

Let the concentration of  $\text{Cu}^{2+}$  be  $y \text{ mol dm}^{-3}$   
 $(y)(5.495 \times 10^{-8})^2 = 2.2 \times 10^{-20}$   
 $y = 7.29 \times 10^{-6} \text{ mol dm}^{-3}$

[2]

- (ii) The industrial wastewater is treated at pH 6.74. Using your answer in (b)(i), deduce if the wastewater is safe for discharge to sanitary sewage for further treatment?

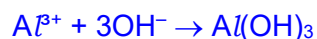
Allowable limit of  $\text{Cu}^{2+} = 1 \text{ mg} / \text{L} = 1 \times 10^{-3} \text{ g dm}^{-3}$   
 $= 1.575 \times 10^{-5} \text{ mol dm}^{-3}$

Yes, it is safe as the allowable limit is larger than  $[\text{Cu}^{2+}]$  present in the discharge at pH 6.74.

[1]

- (c) There may be difficulty in removing  $\text{Al}^{3+}$  ion from the wastewater when excess sodium hydroxide solution is added.

Explain, with the aid of suitable equation(s), why this is so.



NaOH is added to precipitate  $\text{Al}^{3+}$  ions in the form of  $\text{Al}(\text{OH})_3$ .



However, when excess NaOH is added, concentration of  $\text{OH}^-$  increases, thus

position of equilibrium (1) shifts to the right to form the soluble complex ion

**[1]** in the wastewater and **cannot be precipitated**.

[2]

(d) A sample of the industrial wastewater was found to be pale blue in colour due to contamination by  $\text{Cu}^{2+}$  ions.

(i) Explain why the solution contaminated with  $\text{Cu}^{2+}$  is blue in colour.

$\text{Cu}^{2+}$  has a partially-filled 3d subshell. In the presence of  $\text{H}_2\text{O}$  ligand, the 3d orbitals of  $\text{Cu}^{2+}$  splits into two different energy levels. A 3d electron in the lower energy d orbital absorb light energy corresponding to the wavelengths for orange light, and is promoted to a higher energy d orbital. The remaining wavelengths are transmitted and the complementary blue colour is observed. [3]

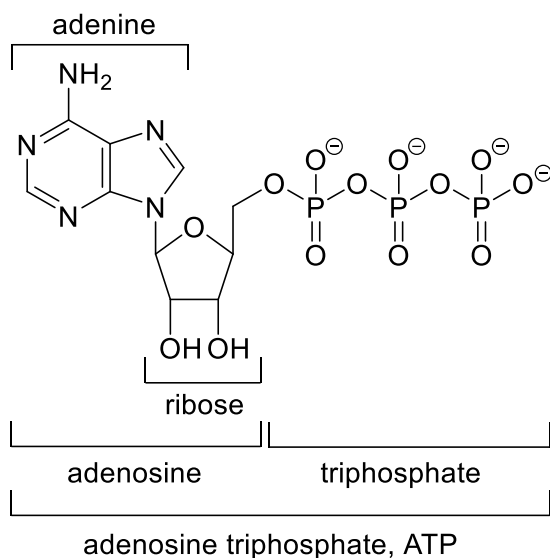
(ii) A student took a sample of the solution and added excess concentrated hydrochloric acid. State the type of reaction and describe any observations. Construct a balanced equation for the reaction.

The blue copper(II) solution will turn green.  
Ligand exchange reaction has occurred due to high concentration of  $\text{Cl}^-$  ligand which displaces the water ligand in the hexaaquacopper(II) complex.  

$$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$$
 [3]

[total: 14]

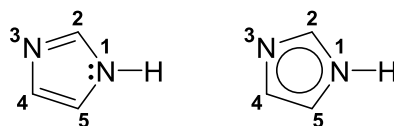
- 5 Energy is crucial for life and bodily functions, stored in the form of adenosine triphosphate, ATP. Renown as “energy currency”, ATP consists of a base, adenine, attached to ribose, to which is attached to a triphosphate group, as shown in Fig. 5.1.



**Fig. 5.1**

- (a) Adenine is made up of a six-membered pyrimidine ring fused with a five-membered imidazole ring, both of which are aromatic and planar.

The imidazole ring specifically contains six  $\pi$  electrons and can exist as an imidazole molecule. Two representations of imidazole molecule are shown in Fig. 5.2.



**Fig. 5.2**

Nitrogen atoms undergo the same type of hybridisation as carbon atoms.

- (i) By reference to orbital overlap and the hybridisation of the nitrogen and carbon atoms, suggest how the  $\sigma$  and  $\pi$  bonds are formed in an imidazole molecule.

The one C–C  $\sigma$  bonds and four C–N  $\sigma$  bonds of the 5-membered ring are formed from head-on overlap of singly filled  $sp^2$  hybrid orbitals on the C and N atoms. The three C–H bonds and one N–H  $\sigma$  bond on the 5-membered ring are formed from head-on overlap of singly filled s orbital of H with  $sp^2$  hybrid orbitals on the C and N, respectively.

The  $\pi$  bonds are formed from side-on overlap of the five contiguous p-orbitals, four singly filled on each of the C and N3 and one filled on N1, in a cyclic manner within the 5-membered ring.

..... [3]

- (ii) An imidazole molecule is amphoteric as it can function both as an acid and a base.

By considering your answer in (a)(i) and its structure or otherwise, suggest and explain:

- The acidic proton is the H atom bonded to N1, not H atoms bonded to carbon atoms.
- N3 acts as the base.

The H bonded to N1 is partially positively charged as it is bonded to the more electronegative N atom, hence more likely to be released as  $H^+$ .

C–H bonds are non-polar and less likely to release acidic protons.

OR N–H bond is weaker than C–H bond (bond energy based on Data Booklet)

OR negative charge of N, not C, can be delocalised into the resonance stabilised anion since lone pair of electrons of C is perpendicular to delocalised  $\pi$  electron cloud

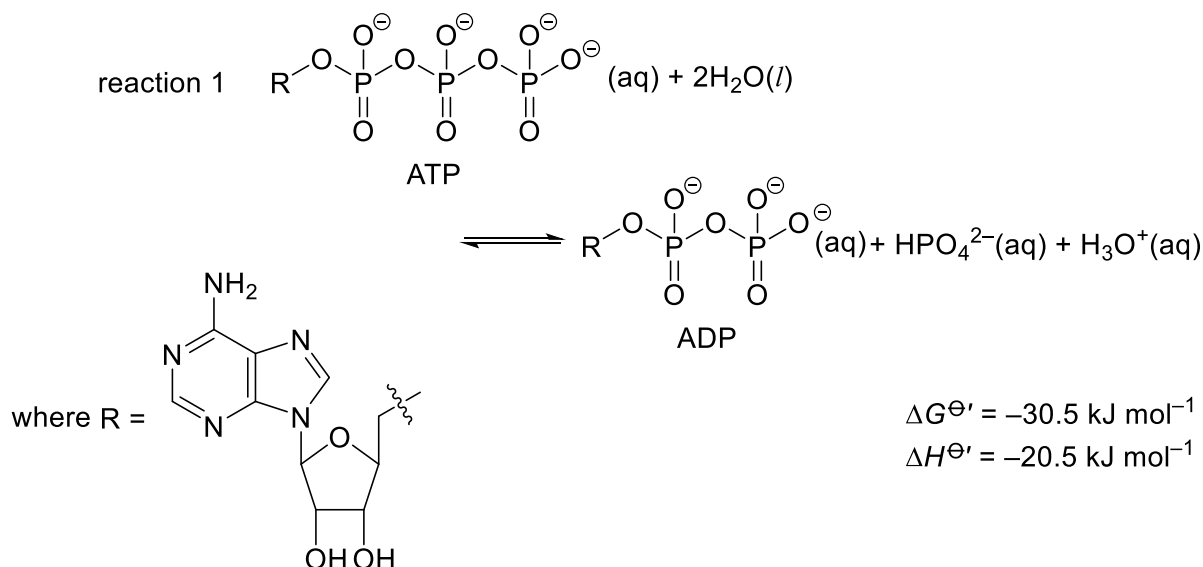
OR consider relative stability of conjugate base whereby negative charge is more likely to reside on N rather than C since N is more electronegative.

The lone pair of electrons of N3 is available for protonation as it is perpendicular to the delocalised  $\pi$  electron cloud, thus it can act as a base.

..... [2]



ATP hydrolysis breaks a high-energy P–O bond, releasing energy and forming ADP and  $\text{HPO}_4^{2-}$ , and is reversible under suitable conditions in reaction 1. The biochemical standard condition (as annotated by the superscript of  $\ominus'$ ) applies here where concentrations of all species are defined to be at  $1 \text{ mol dm}^{-3}$  at pH 7.0, at  $37^\circ\text{C}$ .



(b) The mechanism of the hydrolysis of ATP proceeds via the following stages:

1. Similar to nucleophilic addition, a nucleophilic attack of water on a phosphorus atom of the terminal phosphate unit while breaking the P=O  $\pi$  bond, forming intermediate 1.
2. The negative charge of the oxygen atom in intermediate 1 is then conferred to reforming of the  $\pi$ -bond in the P=O while another P–O bond involving the phosphorus atom of the terminal phosphate unit is cleaved to form intermediate 2 and ADP.
3. Another water molecule abstracts a proton from intermediate 2.

(i) Suggest why a water molecule is a nucleophile.

The presence of two lone pairs of electrons on the oxygen atom of the water molecule. enables it to attack electron-deficient regions to form new covalent bonds. [1]

- (ii) Complete Fig. 5.3 to suggest the mechanism for this reaction for stages 1 and 2 only. Show the displayed structure of intermediate 2, relevant dipoles, relevant lone pairs of electrons and the movement of electrons by using curly arrows. [3]

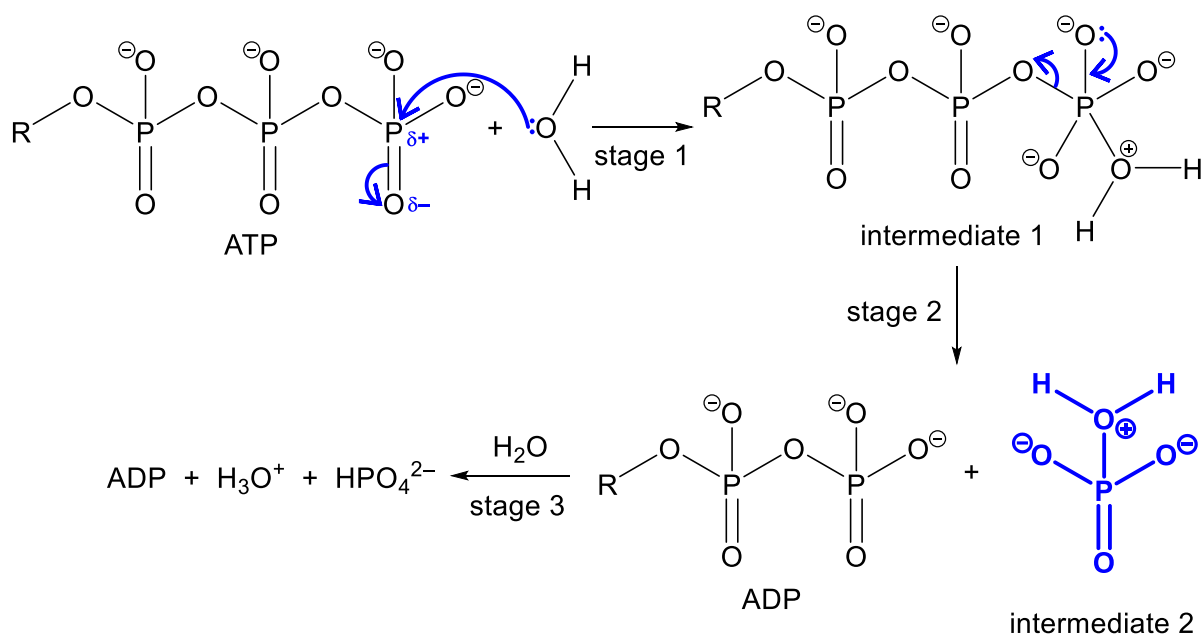


Fig. 5.3

- (c) Calculate the entropy change of reaction,  $\Delta S^{\ominus}$ , at 37 °C and comment on the sign of  $\Delta S^{\ominus}$  obtained.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta S^{\ominus} = (-20.5 - (-30.5)) \div (37+273) = \underline{+0.0322 \text{ kJ mol}^{-1}}$$

There is increase in amount of aqueous particles which allows more ways for particles and their energies to distribute amongst themselves, resulting in increase in entropy. [2]

- (d) Physiological conditions vary depending on the organism, the specific tissue or cell compartment, and the current energy needs for metabolic and other reactions. Table 5.1 shows the concentrations of ATP, ADP and  $\text{HPO}_4^{2-}$  for various physiological conditions of organism.

Table 5.1

physiological condition of organism	ATP concentration / $\text{mol dm}^{-3}$	ADP concentration / $\text{mol dm}^{-3}$	$\text{HPO}_4^{2-}$ concentration / $\text{mol dm}^{-3}$
standard condition	1	1	1
human – resting muscle	$8 \times 10^{-3}$	$9 \times 10^{-6}$	$4 \times 10^{-3}$
human – muscle recovery from severe exercise	$8 \times 10^{-3}$	$7 \times 10^{-6}$	$1 \times 10^{-3}$

- (i) Other than concentration to be  $1 \text{ mol dm}^{-3}$ , state another condition specified by the symbol  $^\ominus$  when the enthalpy change, entropy change and Gibbs free energy for a reaction are described at 298 K.

The partial pressure of all gaseous species must be at 1 bar...... [1]

- (ii) By considering Table 5.1 or otherwise, suggest why the standard condition is not applicable to most physiological conditions.

The standard condition defines that for reactions (such as reaction 1) involving  $\text{H}^+$  ions, the resultant pH would be 0. This is not appropriate for living systems where most cells have a physiological pH close to the neutral pH of 7.

**OR** The standard condition is not applicable in cells where the concentrations of ATP, ADP,  $\text{P}_i$  are the magnitude of mM, much lower than the standard concentration of  $1 \text{ mol dm}^{-3}$ ......

.....

..... [1]

- (iii) Equation 1 can be used to compute the actual Gibbs free energy change,  $\Delta G$  due to ATP hydrolysis under physiological condition.

Equation 1  $\Delta G = \Delta G^{\ominus'} + RT \ln Q_c$

where  $Q_c$  refers to the reaction quotient which has the same expression as  $K_c$ .

Using equation 1, Table 5.1 and the *Data Booklet*, calculate the Gibbs free energy change,  $\Delta G$  due to ATP hydrolysis in reaction 1 for human muscle of athletes recovering from severe physical exertion at 37 °C at pH = 7.4.

$$\begin{aligned}\Delta G &= \Delta G^{\ominus'} + RT \ln Q_c \\ &= \Delta G^{\ominus'} + RT \ln \frac{[\text{ADP}][\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{ATP}]} \\ &= -30500 + 8.31 \times (37 + 273) \times \ln \frac{(7 \times 10^{-6})(1 \times 10^{-3})(10^{-7.4})}{8 \times 10^{-3}} \\ &= -110329 \text{ J mol}^{-1} \\ &= -110 \text{ kJ mol}^{-1}\end{aligned}$$

[2]

In the presence of magnesium ions, the Gibbs free energy change of reaction 1 changes. This is shown in Fig. 5.4.

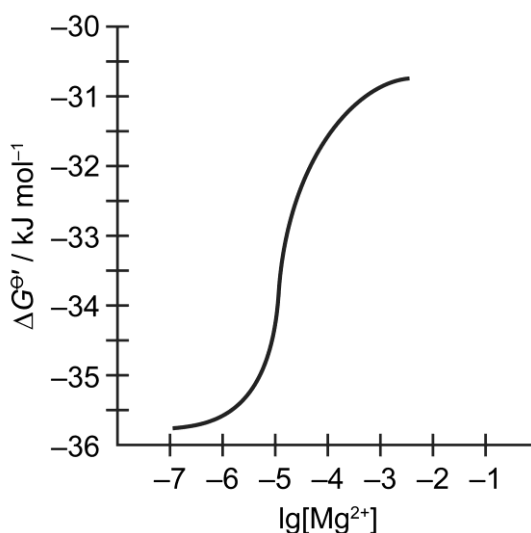


Fig. 5.4

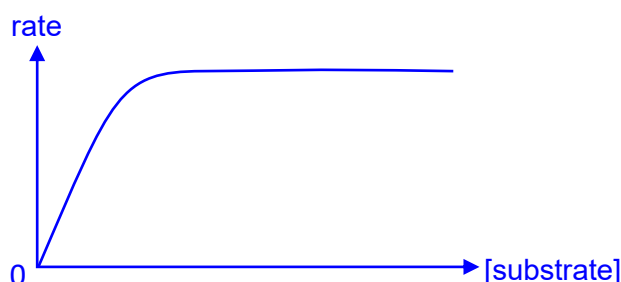
- (e) (i) Based on Fig. 5.4, describe how Gibbs free energy change varies with increasing concentration of magnesium ions.

As concentration of  $\text{Mg}^{2+}$  increases, the Gibbs free energy change becomes less negative. [1]

- (ii) ATP can form several complexes with magnesium ions such as the  $[\text{MgATP}]^{2-}$  complex. The  $[\text{MgATP}]^{2-}$  complex serves as the substrate for ATPase, the enzyme that catalyses reaction 1.

The rate of reaction 1 using a fixed amount of ATPase is investigated. Experiments are performed using different concentrations of  $[\text{MgATP}]^{2-}$  complex (substrate) and the rate of each reaction is measured.

Sketch a graph to describe the relationship between the rate of the reaction and substrate concentration, using a fixed amount of ATPase enzyme, in this reaction. Explain your reasoning.



When [substrate] is low, additional substrate is able to bind to an active site on the enzyme and react, hence reaction is first order w.r.t. substrate.

At high [substrate], active sites are saturated. No active sites for additional substrate to bind. Hence reaction becomes zero order w.r.t. substrate.

.....  
 ..... [2]

[Total: 18]