Victoria Junior College
2021 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

1 The table below shows the fifth to eighth ionisation energies of two consecutive elements, **X** and **Y** in the second period of the Periodic Table.

successive ionisation energies / kJ mol^{-1}	5th	6th	7th	8th
X	10990	13330	71330	84080
Y	11020	15160	17870	92040

(a) **(i)** With the aid of an equation, define the term *first ionisation energy* with reference to **X**. [2]

First ionisation energy of X is the amount of energy required to remove one mole of electrons from one mole of X gaseous atoms, producing one mole of gaseous X^+ ions.

$$X(g) \rightarrow X^+(g) + e^-$$

(ii) State and explain the group number of **X**. [1]

Group 16. There is a big jump from 6th to 7th IE, indicating that the 7th electron is removed from the inner principal quantum shell [OR there are 6 valence electrons].

(b) **(i)** Write down the full electronic configurations of $\mathbf{X}^+$ and $\mathbf{Y}^+$. [1]

X^+: $1s^2 2s^2 2p^3$
Y^+: $1s^2 2s^2 2p^4$

(ii) Hence, explain which element has a less endothermic second ionisation energy. [2]

Y has a less endothermic second ionisation energy. It is easier to remove a paired 2p electron in Y^+ due to the presence of interelectronic repulsion between electrons in the same orbital.

(c) Boron is another Period 2 element which reacts vigorously with fluorine to form boron trifluoride, BF_3, an important reactant in organic syntheses.

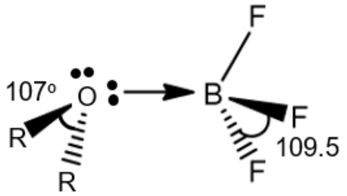
Boron trifluoride is a very reactive gas and it is hard to handle at room temperature. It can be converted to a liquid compound which is easily stored by reacting it with diethyl ether in the mole ratio of 1:1.

Diethyl ether can be represented by the formula ROR, where –R represents the ethyl group.

(i) Explain why boron trifluoride can form a compound with diethyl ether. [2]

ROR has a lone pair of electrons on O while the B in BF_3 has a vacant orbital, hence, B can accept lone pair of electrons to form a stable octet structure via dative bond formation.

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



Structure should include

- **Correct structure with wedge and hash bonds**
- **Dative bond from O to B**
- **Around B: tetrahedral, 109.5°**
- **Around O: trigonal pyramidal, 107°**

[Total: 10]

S2 **(a)** *Use of the Data Booklet is relevant to this part of the question.*

Xenon hexafluoride, XeF_6 was one of the first noble gas compounds synthesised. XeF_6 reacts with the silicon dioxide, SiO_2 in glass to form liquid xenon oxytetrafluoride, $XeOF_4$ and gaseous silicon tetrafluoride, SiF_4 as shown by the equation below:

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

(i) An unknown amount of XeF_6 was allowed to react with SiO_2 in a 2 m^3 closed vessel at 25 °C. When all the XeF_6 has reacted, a pressure of 0.505 kPa was measured in the vessel.

Assuming that the gas inside the vessel behaves ideally, calculate the amount of XeF_6 reacted in the vessel. [2]

Only gaseous SiF_4 exerts a pressure of 0.505 kPa at the end of the reaction.

$PV = nRT$
$0.505 \times 10^3(2) = n(8.31)(25 + 273)$
$n = 0.408$ mol

Hence, amount of XeF_6 reacted = 2 x 0.408
= 0.816 mol

(ii) Hence, calculate the mass of XeF_6 reacted. [1]

Mass of XeF_6 reacted
= 0.816 (131.3 + 19.0(6))
= 200 g

(b) In a given vessel of a fixed volume, N_2O_5 gas decomposed to NO_2 and O_2 as shown below at 50 °C.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The rate equation for this thermal decomposition is as follows.

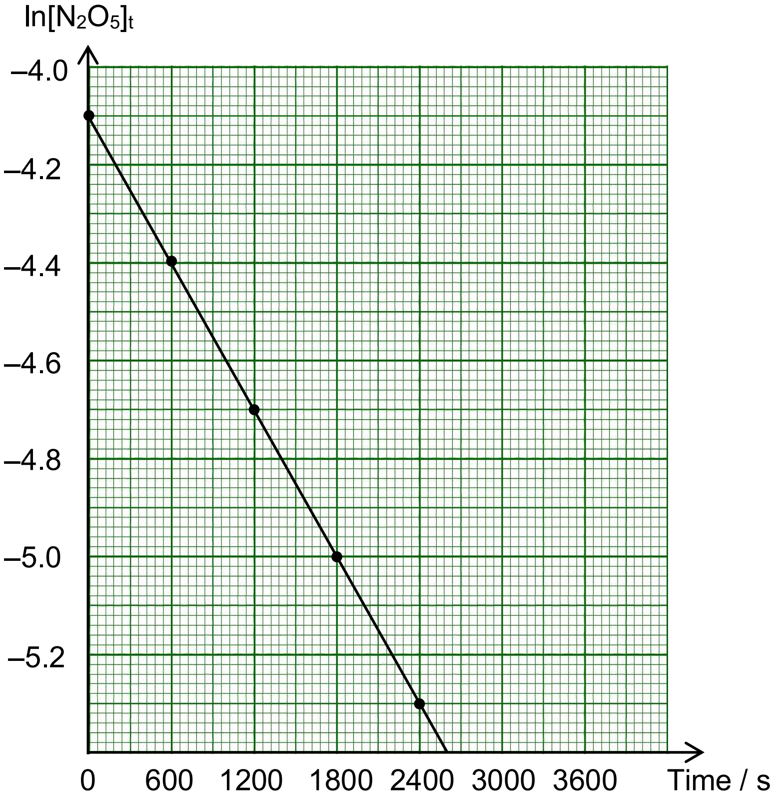
$$\text{Rate} = k[N_2O_5]$$

Theory shows that under the conditions of the experiment, the following relationship between the concentration of N_2O_5 and time is as follows.

equation 1 $\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_{initial}$

where $[N_2O_5]_t$ = concentration of N_2O_5 present at time t
k = rate constant

(i) The following graph of $\ln[N_2O_5]_t$ against t is plotted with the data obtained from the experiment.



With the help of equation 1 and the graph above, determine

I. the initial concentration of N_2O_5 [1]

From the graph, $\ln[N_2O_5]_{initial} = -4.1$
$[N_2O_5]_{initial} = 1.66 \times 10^{-2}$ mol dm^{-3}

II. rate constant, k, including its units [1]

k = –gradient = –(–5.0 + 4.1) / 1800
= 5.00×10^{-4} s^{-1}

(ii) It is known that the rate of the reaction doubles with every 10 °C rise in temperature.

Calculate the initial rate of the thermal decomposition of N_2O_5 when the volume of vessel is halved at 70 °C.

[2]

Rate = $k[N_2O_5]$ = $5.00 \times 10^{-4} \times 4 (1.66 \times 10^{-2} \times 2)$
= 6.64×10^{-5} mol dm^{-3} s^{-1}

(c) In another experiment, O_2 reacts with NO as follows.

$$O_2 + 2NO \rightarrow 2NO_2$$

(i) Using the following data, determine the order of reaction with respect to O_2 and NO. Hence, write down the rate equation for the reaction.

experiment	$[O_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}

[2]

Comparing 1 and 2, when $[O_2]$ is doubled, initial rate is doubled. Hence, first order wrt O_2.
Comparing 1 and 3, when [NO] is doubled, initial rate is increased by four times. Hence, second order wrt NO.
Rate = $k[O_2][NO]^2$

(ii) The following relationship can be used to calculate the activation energy of the reaction between O_2 and NO:

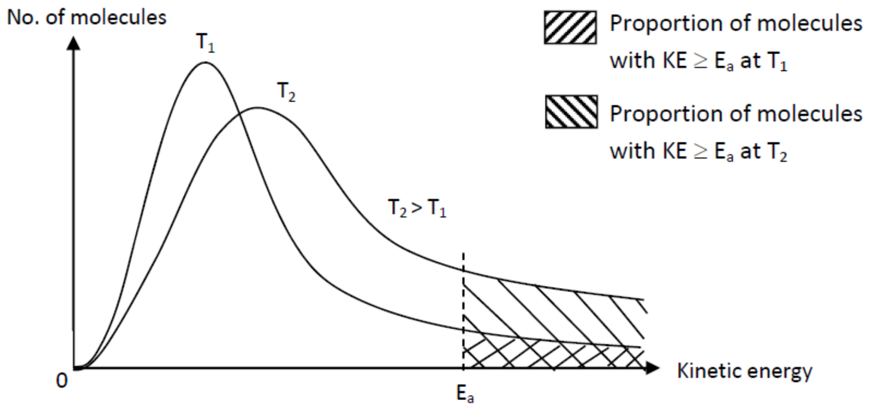
$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where *k* = rate constant at the respective temperature in Kelvins.

Calculate the activation energy of the reaction if the values of the rate constants are 7.00×10^{-3} and 9.21×10^{-3} at 25 °C and 60 °C respectively. Include the correct units in your answer. [2]

$\ln (9.21 \times 10^{-3} / 7.00 \times 10^{-3}) = (-E_a/8.31)(1/333 - 1/298)$
E_a = 6460 J mol^{-1} = 6.46 kJ mol^{-1}

(iii) With an appropriate sketch of the Boltzmann distribution, explain why a rise in temperature increases the value of rate constant, *k*. [2]



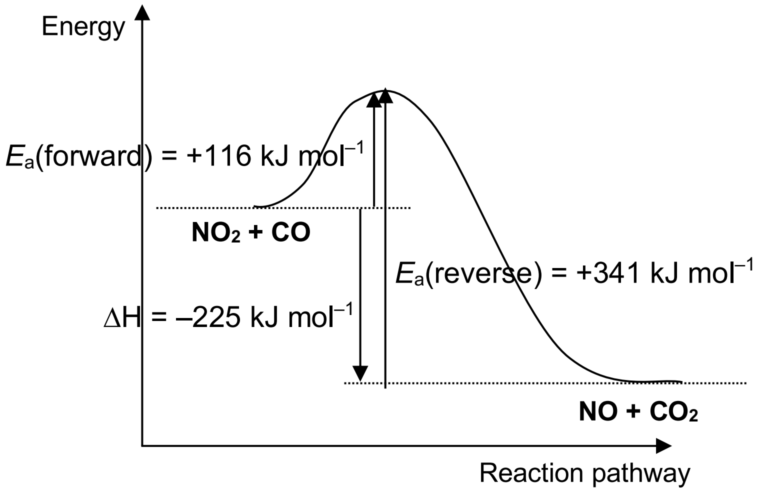
At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases. Thus, frequency of effective collision increases, rate of reaction increases and hence rate constant increases.

(iv) NO_2 produced in the reaction in **(c)** reacts with CO as follows:

$NO_2 + CO \rightleftharpoons NO + CO_2$; $\Delta H = -225$ kJ mol^{-1}

Given that the activation energy for the forward reaction is +116 kJ mol^{-1}, sketch a **fully labelled** energy profile diagram for this reaction. Indicate clearly on the diagram the value of the activation energy for the reverse reaction.

[2]



- **Correct labelling of axes**
- **Correct shape showing negative ΔH**
- **Correct labelling of reactants and products**
- **Correct labelling of E_a(reverse) with its value indicated**

[15 marks]

3 The following data refer to the Haber Process for the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

The table below shows the percentage of ammonia by volume in equilibrium mixtures at various temperatures and pressures. In all cases, N_2 and H_2 were mixed in a 1:3 molar ratio.

pressure / atm	temperature		
	300 °C	400 °C	500 °C
1	2.18	0.44	0.13
10	14.7	3.85	1.21
100	51.2	25.1	10.4

(a) With reference to the data above, explain how changes in temperature and pressure affect the percentage of NH_3 in the equilibrium mixture.

Increase in temperature favour endothermic reaction.
Backward reaction is endothermic hence an increase in temperature results in a decrease in the % of NH_3.
An increase in pressure favours the reaction that produces less number of moles of gas.
Forward reaction produces less number of moles of gas and hence an increase in pressure results in an increase in the % of NH_3.

[2]

(b) Calculate the partial pressure of each gas present in the equilibrium mixture at 100 atm and 400°C.

Hence determine K_p at 400°C.

At 100 atm and 400°C, % NH_3 = 25.1

P_{NH_3} = 0.251×100 = **25.1 atm**
P_{N_2} = $\frac{1}{4}(1 - 0.251) \times 100$ = **18.7 atm**
P_{H_2} = $\frac{3}{4}(1 - 0.251) \times 100$ = **56.2 atm**

K_p = $(P_{NH3})^2 / (P_{H2})^3(P_{N2})$
= $25.1^2 / (18.7 \times 56.2^3)$
= 1.90×10^{-4} atm^{-2}

[2]

(c) Hydrogen halides show clear trends in the H–X bond energy where X = C*l*, Br and I.

(i) With reference to the *Data Booklet*, predict and explain the trend in thermal stability of the hydrogen halides from HC*l* to HI.

Down the group, H–X bond energy decreases from 431 to 299 kJ mol^{-1}.

This is due to the increasing radius of the halogen atom, which causes a poorer extent of overlap of orbitals between H and X. This leads to the H−X bond becoming longer and weaker, and hence less energy is required to break the H−X bond. Hence, thermal stability decreases from HC*l* to HI.

[2]

(ii) Hydrogen halides behave as weak acids in liquid ethanoic acid, dissociating to different extents. Write an equation to show how HX dissociates in ethanoic acid.

$HX + CH_3CO_2H \rightleftharpoons CH_3CO_2H_2^+ + X^-$

[1]

(iii) Rank the pK_a values of the three hydrogen halides in ethanoic acid in decreasing order. Explain your answer.

It becomes easier to dissociate HX down the group as H–X bond energy decreases. Hence HI is the strongest acid.
K_a of acids: HC*l* < HBr < HI
pK_a of acids: HC*l* > HBr > HI

[2]

(iv) Using common ion effect principle, suggest why the hydrogen halides are weaker acids in ethanoic acid than in water.

Since ethanoic acid is a stronger acid than water, it will partially dissociate into H^+ ion in aqueous state, hence, causing the position of equilibrium of $HX \rightleftharpoons H^+ + X^-$ to shift left (or suppress the dissociation of HX) by common ion effect.

[1]

[Total: 10]

S4 Petroleum or crude oil is a complex mixture of organic compounds consisting of mainly hydrocarbons, with small quantities of other organic compounds containing nitrogen, oxygen or sulfur.

In the refining of crude oil, this mixture is partly separated by fractional distillation. Long chain alkanes obtained from the fractional distillation of crude oil can be converted to the more useful shorter chain alkanes and alkenes via a process called cracking.

The information below is related to the thermal cracking of 1 mole of the alkane $C_{15}H_{32}$.

- Four products **P**, **Q**, **R** and **S** in the molar ratio 2:1:1:1 were obtained.
- **P** is ethene.
- **Q** has a relative molecular mass of 42.0.
- **R** has a relative molecular mass of 56.0 and exists as a pair of cis-trans isomers.

(a) **(i)** Suggest the structural formulae of **Q**, **R** and **S**.

Q: CH_2=$CHCH_3$
R: CH_3CH=$CHCH_3$
Number of carbon for S = 4
S: $CH_3CH_2CH_2CH_3$ or $CH(CH_3)_3$

[3]

(ii) Explain, with reference to its structure, why **R** can exist as a pair of cis–trans isomers.

R has a C=C bond which resists rotation and two different groups attached to each alkene C.

[1]

(b) The process of thermal cracking proceeds via a free radical mechanism. The following are reactions involved when propane undergoes thermal cracking.

reaction	equation
1	$CH_3CH_2CH_3 \rightarrow \bullet CH_3 + \bullet CH_2CH_3$
2	$CH_3CH_2CH_3 \rightarrow \bullet H + \bullet CH_2CH_2CH_3$
3	$\bullet CH_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \bullet CH_2CH_2CH_3$
4	$\bullet CH_2CH_3 \rightarrow \bullet H + CH_2{=}CH_2$
5	$\bullet CH_3 + CH_2{=}CH_2 \rightarrow \bullet CH_2CH_2CH_3$
6	$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$
7	$2\,\bullet CH_2CH_3 \rightarrow CH_3CH_3 + CH_2{=}CH_2$

(i) Reactions 1 and 2 are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

Reaction 1 is more likely to occur as it is easier to break a C-C bond (350 kJ mol^{-1}) compared to a C-H bond (410 kJ mol^{-1})

[1]

(ii) From reactions 3 to 7, identify those which may be termed propagation steps in the mechanism.

Reaction 3, 4 and 5

[1]

(iii) Which gas, if detected in the product mixture, would offer support for the occurrence of both reactions (2) and (4)?

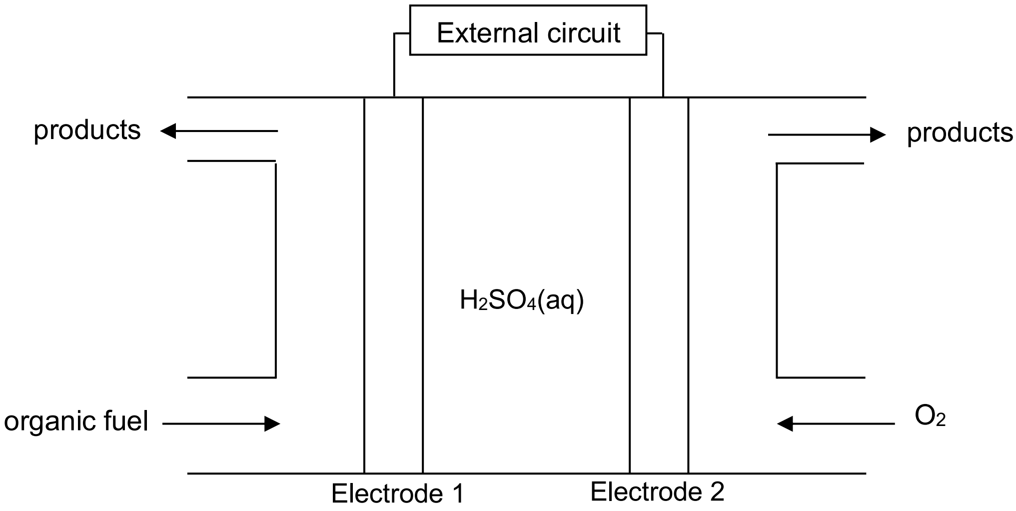
Hydrogen

[1]

(c) Alternative energy sources that are renewable and contribute less to global warming are rapidly gaining in popularity as natural gas and crude oil are depleting at a fast rate.

As an alternative energy source, direct liquid fuel cell (DLFC) is one of the leading fuel cell types due to their great features of superior energy density, modest configuration and small size in fuel container. Commercially used liquid fuel types are prepared using alcohols, such as methanol or ethanol, glycol, and acids.

The following diagram illustrates the parts of a typical DLFC. Organic fuel is supplied to electrode 1 and oxygen is supplied to electrode 2 simultaneously. The electrons produced at electrode 1 pass around the external circuit to electrode 2. The protons formed from the oxidation move through the conducting polymer electrolyte to electrode 2, where they react with oxygen to produce water.



While fuel cells which use organic fuel such as liquid alcohols pose no storage problem, they emit carbon dioxide, thus countering the move to reduce carbon footprint. Research was done to assess the viability of the oxidation of propan-2-ol to propanone as a potential organic fuel cell reaction.

(i) Construct ion-electron equations for the reactions at electrode 1 and electrode 2 respectively.

Electrode 1 $CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e^-$
Electrode 2 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

[2]

(ii) Hence construct the equation for the overall reaction.

$2CH_3CH(OH)CH_3 + O_2 \rightarrow 2CH_3COCH_3 + 2H_2O$

[1]

(iii) The $E^\ominus$ of the $CH_3COCH_3/CH_3CH(OH)CH_3$ electrode reaction is –0.03 V. By using suitable data from the *Data Booklet,* calculate the $E^\ominus_{cell}$ for the reaction.

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$= 1.23 - (-0.03)$
$= 1.26$ V

[2]

(iv) State how $E^\ominus_{cell}$ and $\Delta G^\ominus_{cell}$ will change when twice the amount of the reactants as given in the overall reaction in **(c)(ii)** is used for the reaction.

No change to $E^\ominus_{cell}$
$\Delta G^\ominus_{cell}$ is doubled

[1]

(v) Pyrogallol solution is an organic compound that absorbs oxygen efficiently.

Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$
When a small amount of pyrogallol solution is added, it decreases the partial pressure of O_2. Hence equilibrium above will shift to the left to increase partial pressure of O_2.
$E^\ominus_{red}$ will be less positive and hence overall $E^\ominus_{cell}$ value will be less positive.

[2]

[Total: 15]

5 **(a)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure. It is formed from S_8 and Cl_2.

(i) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps. The first step involves the formation of disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write an equation to represent the second step.

$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$

[1]

Some chemists speculate that the intermediate is not S_2Cl_2 but **K**. **K** shares the same elemental mass percentages as sulfur dichloride, SCl_2 but it has a molar mass of 206.2 g mol^{-1} instead.

(ii) State the molecular formula of **K**.

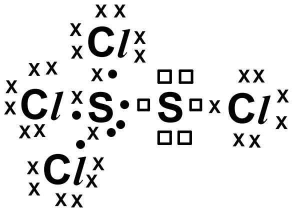
S_2Cl_4

[1]

(iii) The following is known about the structure of **K**:

- There is more than one central atom present.
- All the central atoms are sulfur atoms and possess at least one lone pair
- The shape about each central atom is different.

Draw a dot-and-cross diagram for **K**.



[1]

(b) Compounds **C** and **D** are chlorides of Period 3 elements. Both **C** and **D** exist in the solid state at room temperature.

When excess water was added to a sample containing 0.100 mol of **C**, an acidic solution was obtained**.** The resulting solution required 0.500 mol of silver nitrate for complete precipitation.

On the other hand, when excess water was added to a sample containing 0.100 mol of **D**, a neutral solution was obtained.

(i) Identify compounds **C** and **D**.

C is PCl_5 and D is NaC*l*

[2]

(ii) Explain, with the aid of equations, the difference in the pH of the solutions obtained when water is added to **C** and **D**.

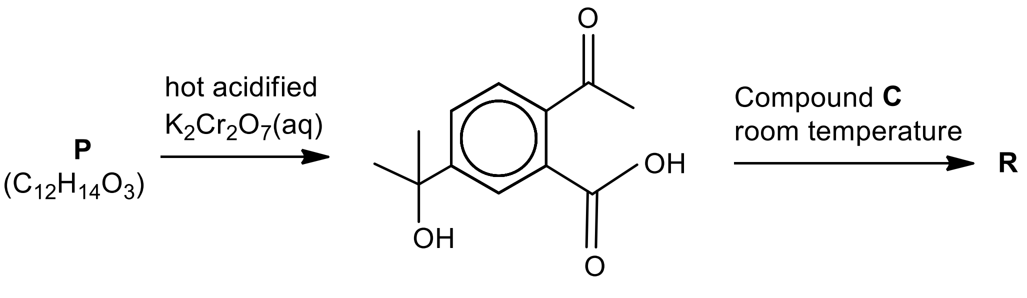
C (PCl_5) has vacant 3d orbitals on phosphorus. Hence, it undergoes hydrolysis when water is added:
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
H_3PO_4 and HC*l* formed cause the solution to be acidic.

D (NaC*l*) undergoes only hydration [OR $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$]
This is due to Na^+ having low charge density.
Since there is no hydrolysis, the solution remains neutral.

[2]

(c) Compound **C** is commonly used as a reagent in organic chemistry reactions.

(i) Consider the scheme below which involves **C** in one of the steps:

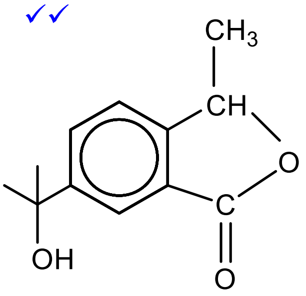


Q ($C_{12}H_{14}O_4$)

P does not react with sodium carbonate or Brady's reagent.

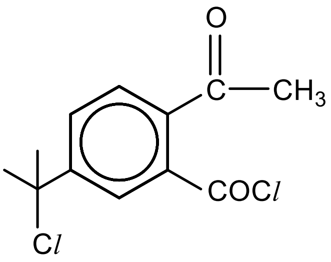
Suggest structures for **P** and **R**.

✓✓



P

✓✓

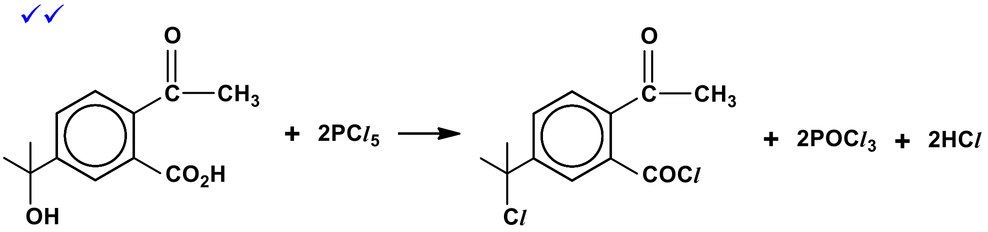


R

[2]

(ii) Write a balanced equation for the reaction between **Q** and **C** to form **R**.

✓✓



[1]

(d) [Use of the *Data Booklet* is relevant to this part of the question].

Compound **Q** is a solid which can be neutralised by aqueous NaOH. An experiment was carried out to determine the enthalpy change of the reaction. 5.00 g of **Q** was added to 40.0 cm^3 of 0.800 mol dm^{-3} NaOH(aq) in a Styrofoam cup and the reaction mixture was stirred. The temperature rose from 25.0°C to 31.2°C.

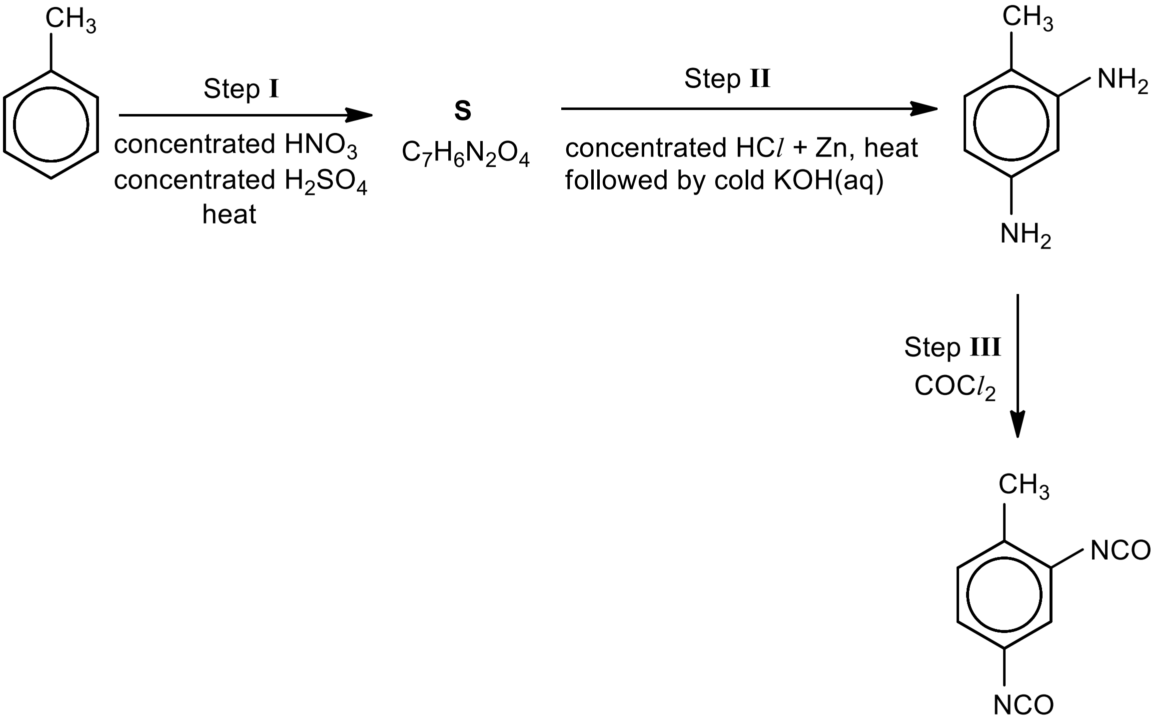
Determine the enthalpy change per mole of water formed in the reaction.

Heat evolved = $40.0 \times (31.2 - 25.0) \times 4.18 = 1036$ J = 1.036 kJ
$RCO_2H(s) + NaOH(aq) \rightarrow RCO_2^-Na^+(aq) + H_2O(l)$
Initial $n_Q = 5 / 222.0 = 0.02252$ mol
Initial $n_{NaOH} = (40.0 / 1000) \times 0.800 = 0.0320$ mol
Hence, Q is the limiting reagent.
$n_{water} = 0.02252$ mol
$\Delta H_{reaction} = -1.036 / 0.02252 = -46.0$ kJ mol^{-1}

[2]
[Total: 12]

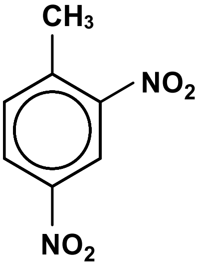
6 **(a)** Compounds containing the isocyanate functional group, –NCO, are important industrial chemicals. They react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

Shown below is the synthesis of a diisocyanate from methylbenzene:



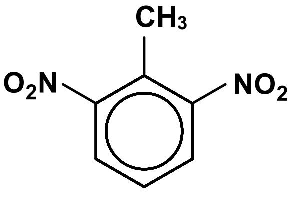
a diisocyanate

(i) Draw the structure of **S**.



[1]

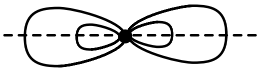
(ii) A number of isomers of **S** is formed in step **I** as side-products. Draw the structure of the side-product formed in the greatest proportion.



[1]

(iii) State the type of hybridisation exhibited by the carbon in the –NCO group and draw the hybrid orbitals around this carbon, showing clearly their shape and alignment.

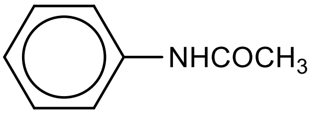
sp hybridisation



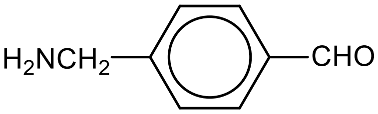
correct shape of orbital
orbitals linearly aligned

[2]

(b) The structures of two organic nitrogen compounds, **T** and **U**, are given below:



T



U

Both compounds exist as solids at room temperature and pressure. They have different basic strengths, which cause them to have different solubility in an aqueous acid solution such as HC*l*(aq).

(i) Which compound, **T** or **U**, is the stronger base? Explain your answer.

<u>U</u> is the stronger base. In T, the <u>lone pair on N is delocalised into the –CO– group</u> (OR into the benzene ring). Hence, lone pair on T is less available for donation to a proton.

[2]

(ii) **T** and **U** are found mixed together in a sample.

By considering your answer in **(b)(i)**, outline briefly a simple method that allows you to separate the two compounds and recover them in their original solid forms. Your method should only make use of normal chemicals and apparatus found in a school laboratory.

<u>Dissolve</u> the mixture completely in <u>aqueous HC*l* (OR H_2SO_4 OR HNO_3)</u>.
<u>Filter</u> the mixture. Solid <u>T</u> is found in the <u>residue</u> while U is found in the filtrate in the protonated form.
Add excess <u>aq NaOH to the filtrate</u> to reform U in the solid state.
<u>Filter</u> the mixture to recover U as the residue.

[2]

(c) In the study of the structure of a polypeptide **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

digestion using the first enzyme	digestion using the second enzyme
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

Deduce the sequence of amino acids in the polypeptide **A**.

Overlapping the fragments, we have:
his-phe-gly
his-phe gly-asp-gly-thr
asp-gly thr-phe-leu
phe-leu-ser
ser-pro-glu
pro-glu

Complete sequence is his−phe−gly−asp−gly−thr−phe−leu−ser−pro−glu

[2]

(d) The structure of a certain tripeptide is given below:

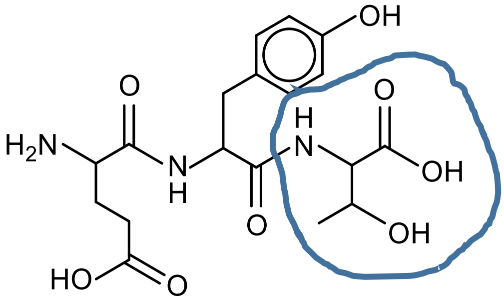


Figure 6.1

It is formed from the amino acids **W**, **X** and **Y**.

Table 6.1 shows the pK_a values of the different functional groups present in each amino acid.

Table 6.1

amino acid	pK_a of α–carboxyl group	pK_a of α–amino group	pK_a of side–chain
W	2.09	9.10	–
X	2.20	9.11	10.07
Y	2.19	9.67	4.25

W and **X** exist mainly as zwitterions at pH 7.0 but **Y** does not.
W rotates plane-polarised light and can exist as four possible stereoisomers.

(i) Circle on Figure 6.1 the part of the tripeptide that originates from **W**.

See Figure 6.1

[Reason: The amino acid that corresponds to the circled part has two chiral centres, hence giving rise to 4 stereoisomers.
It also has a neutral side-chain, which hence does not have a pK_a value.]

[1]

(ii) State what is meant by the term *zwitterion*.

Zwitterion has both positively and negatively charged groups within the same molecule and is electrically neutral.

[1]

(iii) Suggest a pH at which the predominant species of **Y** is a zwitterion using the information in Table 6.1.

3.0 (accept any value between 2.19 and 4.25)

[1]

[Total: 13]