## A-level

## CHEMISTRY

## (7405/2)

Paper 2: Organic and Physical Chemistry

Specimen 2015
Session
Time allowed: 2 hours

## Materials

For this paper you must have:

- the Data Booklet, provided as an insert
- a ruler
- a calculator.


## Instructions

- Answer all questions.
- Show all your working.


## Information

- The maximum mark for this paper is 105 .

Please write clearly, in block capitals, to allow character computer recognition.
Centre number $\square$ Candidate number $\square$
Surname $\square$
Forename(s) $\square$

Candidate signature $\qquad$

Answer all questions.

1 This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in Table 1 were obtained in a series of experiments on the rate of the reaction between compounds $\mathbf{A}$ and $\mathbf{B}$ at a constant temperature.

Table 1

| Experiment | Initial concentration <br> of $\mathbf{A} / \mathbf{m o l ~ d m}^{\mathbf{- 3}}$ | Initial concentration <br> of $\mathbf{B} / \mathbf{~ m o l ~}^{\mathbf{~ d m}}$ | Initial rate <br> $/ \mathbf{~ m o l ~ d m}^{-3} \mathbf{s}^{-1}$ |
| :--- | :---: | :---: | :---: |
| 1 | 0.12 | 0.26 | $2.10 \times 10^{-4}$ |
| 2 | 0.36 | 0.26 | $1.89 \times 10^{-3}$ |
| 3 | 0.72 | 0.13 | $3.78 \times 10^{-3}$ |


| $\mathbf{0}$ | $\mathbf{1}$ | $\mathbf{1}$ Show how these data can be used to deduce the rate expression for the reaction |
| :--- | :--- | :--- | between $\mathbf{A}$ and $\mathbf{B}$.

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The data in Table 2 were obtained in two experiments on the rate of the reaction between compounds $\mathbf{C}$ and $\mathbf{D}$ at a constant temperature.

## Table 2

| Experiment | Initial concentration <br> of $\mathbf{C} / \mathbf{~ m o l ~ d m}^{-3}$ | Initial concentration <br> of $\mathbf{D} / \mathbf{~ m o l ~ d m}^{-3}$ | Initial rate <br> $/ \mathbf{~ m o l ~ d m}^{-3} \mathbf{s}^{\mathbf{- 1}}$ |
| :--- | :---: | :---: | :---: |
| 4 | $1.9 \times 10^{-2}$ | $3.5 \times 10^{-2}$ | $7.2 \times 10^{-4}$ |
| 5 | $3.6 \times 10^{-2}$ | $5.4 \times 10^{-2}$ | To be calculated |

The rate equation for this reaction is

$$
\text { rate }=k[\mathbf{C}]^{2}[\mathbf{D}]
$$

| $\mathbf{0}$ | $\mathbf{1}$ | $\mathbf{2}$ Use the data from experiment $\mathbf{4}$ to calculate a value for the rate constant, $k$, at this l |
| :--- | :--- | :--- | temperature. Deduce the units of $k$.

$$
k=
$$

$\qquad$ Units = $\qquad$

| $\mathbf{0}$ | $\mathbf{1}$. | $\mathbf{3}$ Calculate a value for the initial rate in experiment 5. |
| :--- | :--- | :--- |


| $\mathbf{0}$ | $\mathbf{1}$ | $\mathbf{4}$ The rate equation for a reaction is |
| :--- | :--- | :--- |

$$
\text { rate }=k[\mathrm{E}]
$$

Explain qualitatively why raising the temperature by $10^{\circ} \mathrm{C}$ has a much greater effect on the rate of the reaction than doubling the concentration of $\mathbf{E}$.
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Use the equation $\ln k=\ln A-E_{\mathrm{a}} / R T$ to calculate a value, in $\mathrm{kJ} \mathrm{mol}^{-1}$, for the activation energy of this reaction.

The constant $A=2.57 \times 10^{10} \mathrm{~mol}^{-1} \mathrm{dm}^{3}$. The gas constant $R=8.31 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$.
$\qquad$


2 Butadiene dimerises according to the equation

$$
2 \mathrm{C}_{4} \mathrm{H}_{6} \longrightarrow \mathrm{C}_{8} \mathrm{H}_{12}
$$

The kinetics of the dimerisation are studied and the graph of the concentration of a sample of butadiene is plotted against time. The graph is shown in Figure 1.

Figure 1


| $\mathbf{0}$ | $\mathbf{2}$. $\mathbf{1}$ Draw a tangent to the curve when the concentration of butadiene is |
| :--- | :--- | $0.0120 \mathrm{~mol} \mathrm{dm}^{-3}$.


| $\mathbf{0}$ | $\mathbf{2}$. | $\mathbf{2}$ The initial rate of reaction in this experiment has the value |
| :--- | :--- | :--- | $4.57 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$.

Use this value, together with a rate obtained from your tangent, to justify that the order of the reaction is 2 with respect to butadiene.
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Turn over for the next question

3 Isooctane $\left(\mathrm{C}_{8} \mathrm{H}_{18}\right)$ is the common name for the branched-chain hydrocarbon that burns smoothly in car engines. The skeletal formula of isooctane is shown in Figure 2.

Figure 2


| $\mathbf{0}$ | $\mathbf{3}$. | $\mathbf{1}$ Give the IUPAC name for isooctane. |
| :--- | :--- | :--- | :--- |



Only one answer is allowed.
Completely fill in the circle alongside the appropriate answer.
CORRECT METHOD


WRONG METHODS $\square$
If you want to change your answer you must cross out your original answer as shown.


If you wish to return to an answer previously crossed out, ring the answer you now wish to select as shown.

5


6


7


8


| 0 | 3 | 3 |
| :--- | :--- | :--- | Isooctane can be formed, together with propene and ethene, in a reaction in which one molecule of an alkane that contains 20 carbon atoms is cracked.

Using molecular formulas, write an equation for this reaction.

| $\mathbf{0}$ | $\mathbf{3} .4$ | $\mathbf{4}$ How do the products of the reaction in Question 3.3 show that the reaction is an |
| :--- | :--- | :--- | example of thermal cracking?


| $\mathbf{0}$ | $\mathbf{3}$ | $\mathbf{5}$ | Deduce the number of monochloro isomers formed by isooctane. |
| :--- | :--- | :--- | :--- | :--- |

Draw the structure of the monochloro isomer that exists as a pair of optical isomers.

Number of monochloro isomers $\qquad$
Structure

| $\mathbf{0}$ | $\mathbf{3}$. 6 An isomer of isooctane reacts with chlorine to form only one monochloro |
| :--- | :--- | :--- | compound.

Draw the skeletal formula of this monochloro compound.

| $\mathbf{0}$ | $\mathbf{3} .7$ | $\mathbf{7}$ sample of a monochlorooctane is obtained from a comet. The chlorine in the |
| :--- | :--- | :--- | :--- | monochlorooctane contains the isotopes ${ }^{35} \mathrm{Cl}$ and ${ }^{37} \mathrm{Cl}$ in the ratio $1.5: 1.0$ Calculate the $M_{r}$ of this monochlorooctane.


| 0 | $\mathbf{0}$ | $\mathbf{8}$ | Isooctane reacts with an excess of chlorine to form a mixture of chlorinated |
| :--- | :--- | :--- | :--- | compounds.

One of these compounds contains $24.6 \%$ carbon and $2.56 \%$ hydrogen by mass. Calculate the molecular formula of this compound.


4 Alcohol $\mathbf{A}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}$ undergoes reactions separately with acidified potassium dichromate $(\mathrm{VI})$ and with concentrated sulfuric acid.

| 0 | $\mathbf{4}$ | $\mathbf{1}$ |
| :--- | :--- | :--- |


| $\mathbf{0}$ | $\mathbf{4}$. | $\mathbf{2}$ Draw the structure of the organic product, $\mathbf{B}$, formed when $\mathbf{A}$ is oxidised in the |
| :--- | :--- | :--- | reaction with acidified potassium dichromate(VI).


| $\mathbf{0}$ | $\mathbf{4} \cdot \mathbf{3}$ Two isomeric alkenes, $\mathbf{C}$ and $\mathbf{D}$, are formed when $\mathbf{A}$ is dehydrated in the reaction |
| :--- | :--- | :--- | :--- | with concentrated sulfuric acid.

Name the mechanism for this dehydration reaction.

| 0 | 4 | 4 |
| :--- | :--- | :--- |

Isomer C
Isomer D


| $\mathbf{0}$ | $\mathbf{4} .6$ List alcohol $\mathbf{A}$, product $\mathbf{B}$ and isomer $\mathbf{C}$ in order of increasing boiling point. $. ~ . ~$ |
| :--- | :--- |


| 0 | 4 | 7 |
| :--- | :--- | :--- |
| Draw the structure of the isomer of $\mathbf{A}$ that is not oxidised by acidified |  |  | potassium dichromate(VI).


| $\mathbf{0}$ | $\mathbf{4}$ | 8 | Draw the structure of the isomer of $\mathbf{A}$ that cannot be dehydrated to form an alkene |
| :--- | :--- | :--- | :--- | by reaction with concentrated sulfuric acid.

[1 mark]
$5 \quad$ Figure 3 shows a simplified representation of the arrangement of some amino acids in a portion of a protein structure in the form of an $\alpha$-helix.

Figure 3


| 0 | 5 | 1 | Name the type of protein structure in Figure 3. |
| :--- | :--- | :--- | :--- |

$\qquad$

| $\mathbf{0}$ | $\mathbf{5} .2$ | $\mathbf{2}$ Explain the origin of the interaction represented by the dotted lines in Figure 3. |
| :--- | :--- | :--- |

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$6 \quad$ The tripeptide shown in Figure 4 is formed from the amino acids glycine, threonine and lysine.

Figure 4


| 0 | 6 | 1 |
| :--- | :--- | :--- |
| Draw a separate circle around each of the asymmetric carbon atoms in the |  |  | tripeptide in Figure 4.


| 0 | 6 |
| :--- | :--- |


| $\mathbf{0}$ | $\mathbf{6}$. $\mathbf{3}$ Draw the structure of the species formed when glycine reacts with an excess of |
| :--- | :--- | :--- | bromomethane.


| 0 | 6 | 4 |
| :--- | :--- | :--- |
| Deduce the IUPAC name of threonine. |  |  |


$7 \quad$ Repeating units of two polymers, $\mathbf{P}$ and $\mathbf{Q}$, are shown in Figure 5.
Figure 5


P


Q

Name the type of polymerisation involved.

Monomer

Type of polymerisation

| $\mathbf{0}$ | $\mathbf{7}$. | $\mathbf{2}$ | Draw the structures of two compounds that react together to form polymer $\mathbf{Q}$. |
| :--- | :--- | :--- | :--- |

Structure of compound 1

Structure of compound 2
 Justify your answer.
[3 marks]
Advantage
Justification
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Turn over for the next question

8 The anticancer drug cisplatin operates by reacting with the guanine in DNA.
Figure 6 shows a small part of a single strand of DNA. Some lone pairs are shown.

Figure 6


State the name of the sugar molecule that is attached to the bond at $\mathbf{X}$.

| 0 | 8 | 2 |
| :--- | :--- | :--- | Messenger RNA is synthesised in cells in order to transfer information from DNA. The bases in one strand of DNA pair up with the bases used to synthesise RNA.

Figure 7 shows two bases used in RNA.
Figure 7


Base A


Base B

Suggest which of the bases $\mathbf{A}$ and $\mathbf{B}$ forms a pair with guanine in Figure $\mathbf{6}$ when messenger RNA is synthesised.
Explain how the base that you have chosen forms a base pair with guanine.
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Question 8 continues on the next page

| $\mathbf{0}$ | $\mathbf{8}$. | $\mathbf{3}$ Cisplatin works because one of the atoms on guanine can form a co-ordinate bond |
| :--- | :--- | :--- | :--- | with platinum, replacing one of the ammonia or chloride ligands. Another atom on another guanine can also form a co-ordinate bond with the same platinum by replacing another ligand.

On Figure 6, draw a ring round an atom in guanine that is likely to bond to platinum.

| $\mathbf{0}$ | $\mathbf{8}$ | . | $\mathbf{4}$ |
| :--- | :--- | :--- | :--- | An adverse effect of cisplatin is that it also prevents normal healthy cells from replicating.

Suggest one way in which cisplatin can be administered so that this side effect is minimised.


9 1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

A possible synthesis of 1,4-diaminobenzene from phenylamine is shown in Figure 8.

Figure 8


| $\mathbf{0}$ | $\mathbf{9}$. | $\mathbf{1}$ A suitable reagent for step $\mathbf{1}$ is $\mathrm{CH}_{3} \mathrm{COCl}$ |
| :--- | :--- | :--- |

Name and draw a mechanism for the reaction in step 1.

Name of mechanism $\qquad$
Mechanism

The crude product was dissolved in the minimum quantity of hot water and the hot solution was filtered through a hot filter funnel into a conical flask. This filtration removed any insoluble impurities. The flask was left to cool to room temperature.
The crystals formed were filtered off using a Buchner funnel and a clean cork was used to compress the crystals in the funnel. A little cold water was then poured through the crystals.
After a few minutes, the crystals were removed from the funnel and weighed. A small sample was then used to find the melting point.

Give reasons for each of the following practical steps.

The minimum quantity of hot water was used
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The flask was cooled to room temperature before the crystals were filtered off
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The crystals were compressed in the funnel
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A little cold water was poured through the crystals
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Question 9 continues on the next page

| 0 | 9 | 3 |
| :--- | :--- | :--- | The melting point of the sample in Question 9.2 was found to be slightly lower than a data-book value.

Suggest the most likely impurity to have caused this low value and an improvement to the method so that a more accurate value for the melting point would be obtained.
[2 marks]
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Figure 8 is repeated here to help you answer the following questions.

Figure 8


Step 3


0 9 .4 In an experiment starting with 5.05 g of phenylamine, 4.82 g of purified product were obtained in step 1.

Calculate the percentage yield in this reaction.
Give your answer to the appropriate number of significant figures.

Percentage yield $=$

0 9. 5 A reagent for step 2 is a mixture of concentrated nitric acid and concentrated sulfuric acid, which react together to form a reactive intermediate.

Write an equation for the reaction of this intermediate in step 2.

| 0 | 9 |
| :--- | :--- | Name a mechanism for the reaction in step 2.


| $\mathbf{0}$ | $\mathbf{9}$. | $\mathbf{7}$ Suggest the type of reaction occurring in step 3. |
| :--- | :--- | :--- |


| 0 | 9 | 8 |
| :--- | :--- | :--- |
| Identify the reagents used in step 4. |  |  |

$\qquad$

10 The infrared spectrum (Figure 9) and the ${ }^{1} \mathrm{H}$ NMR spectrum (Figure 10) of compound $\mathbf{R}$ with molecular formula $\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{O}$ are shown.

Figure 9

Transmittance / \%


Figure 10


| $\mathbf{1}$ | $\mathbf{0} \quad$ The relative integration values for the NMR peaks are shown on Figure 10. |
| :--- | :--- |

Deduce the structure of compound $\mathbf{R}$ by analysing Figure 9 and Figure 10. Explain each stage in your deductions.

Use Table A and Table B on the Data Sheet.
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Turn over for the next question

11 Butanone is reduced in a two-step reaction using $\mathrm{NaBH}_{4}$ followed by dilute hydrochloric acid.

| 1 | 1 | 1 | Write an overall equation for the reduction of butanone using $[H]$ to represent the |
| :--- | :--- | :--- | :--- | reductant.

1 1. 2 . By considering the mechanism of the reaction, explain why the product has no effect on plane polarised light.
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12 But-1-ene reacts with a reagent of the form HY to form a saturated compound.

| $\mathbf{1}$ | $\mathbf{2}$. $\mathbf{1}$ Suggest a reagent of the form HY which reacts with but-1-ene. |
| :--- | :--- | :--- |


| $\mathbf{1}$ | $\mathbf{2} .2$ |
| :--- | :--- |

Name of mechanism $\qquad$
Mechanism

| $\mathbf{1}$ | $\mathbf{2}$. | $\mathbf{3}$ Explain how three isomeric products are formed when HY reacts with but-1-ene. |
| :--- | :--- | :--- |

[3 marks]
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END OF QUESTIONS

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