Q1.

This question is about ethanoic anhydride.

In the gas phase, ethanoic anhydride $(CH_3CO)_2O$ decomposes to form ethenone.

The equation is

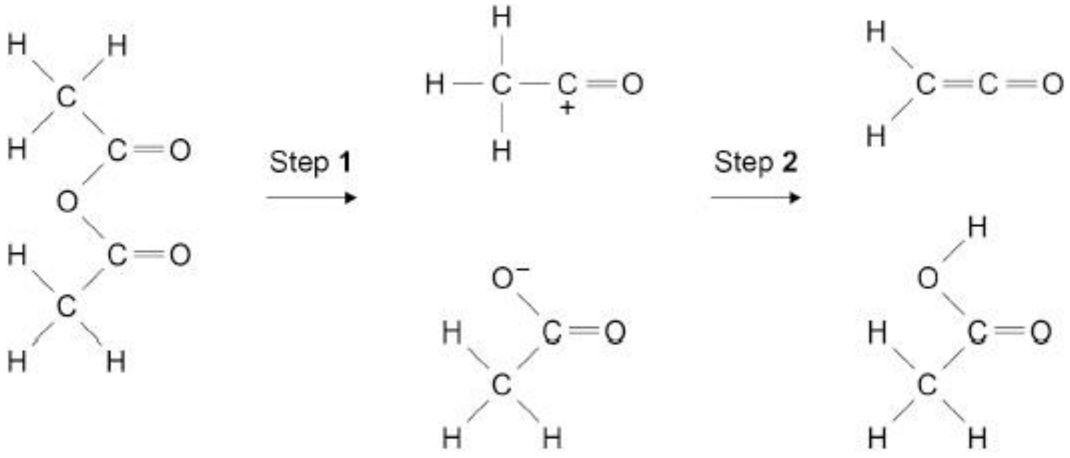
$$(CH_3CO)_2O \rightarrow \underset{\text{Ethenone}}{H_2C{=}C{=}O} + CH_3COOH$$

(a) Ethenone is the simplest member of the ketene homologous series. Ketenes all contain one C=C double bond and one C=O double bond.

Deduce the general formula for the ketene homologous series.

(1)

(b) The figure below shows an incomplete suggested mechanism for the decomposition of ethanoic anhydride.



Complete the mechanism in the figure above by adding three curly arrows and any relevant lone pairs of electrons.

(3)

(c) For a chemical reaction the relationship between the rate constant, *k*, and the temperature, *T*, is shown by the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

For the decomposition of gaseous ethanoic anhydride

the activation energy, $E_a = 34.5$ kJ mol^{-1}
the Arrhenius constant, $A = 1.00 \times 10^{12}$ s^{-1}

At temperature T_1 the rate constant, $k = 2.48 \times 10^{8}$ s^{-1}

Calculate T_1

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

T_1 ______________________ K

(3)

(d) Sketch the Maxwell–Boltzmann distribution of molecular energies for gaseous ethanoic anhydride at temperature T_1 and at a higher temperature T_2

Include a label for each axis, and mark on the appropriate axis a typical position for the activation energy.

Explain why the rate of reaction is faster at T_2

Explanation

____

____

(5)

(Total 12 marks)

Q2.

An acidified solution of butanone reacts with iodine as shown.

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

(a) Draw the displayed formula for $CH_3CH_2COCH_2I$

Give the name of $CH_3CH_2COCH_2I$

Displayed formula

Name ____

(2)

(b) The rate equation for the reaction is

$$rate = k[CH_3CH_2COCH_3][H^+]$$

Table 1 shows the initial concentrations used in an experiment.

Table 1

	$CH_3CH_2COCH_3$	I_2	H^+
Initial concentration / mol dm^{-3}	4.35	0.00500	0.825

The initial rate of reaction in this experiment is 1.45×10^{-4} mol dm^{-3} s^{-1}

Calculate the value of the rate constant, k, for the reaction and give its units.

k ____________________

Units ____________________

(3)

(c) Calculate the initial rate of reaction when all of the initial concentrations are halved.

Initial rate of reaction ____________________ mol dm^{-3} s^{-1}

(1)

(d) An experiment was done to measure the time, *t*, taken for a solution of iodine to react completely when added to an excess of an acidified solution of butanone.

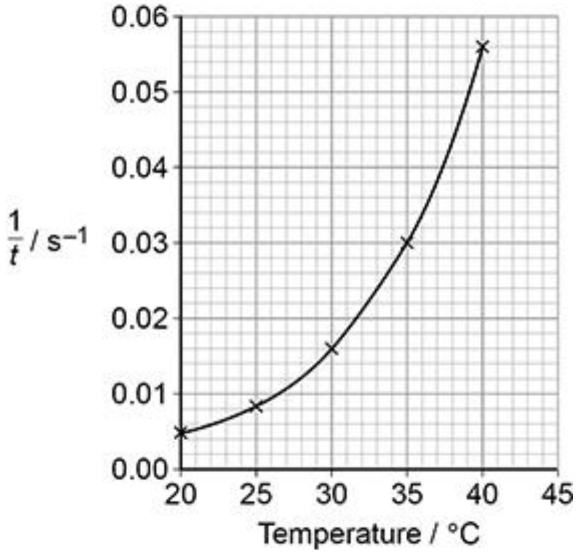
Suggest an observation used to judge when all the iodine had reacted.

____

____

The experiment was repeated at different temperatures.

The graph below shows how $\frac{1}{t}$ varied with temperature for these experiments.



(1)

(e) Describe and explain the shape of the graph above.

(3)

(f) Deduce the time taken for the reaction at 35 °C

Time ______________ s

(1)

(g) For a different reaction, **Table 2** shows the value of the rate constant at different temperatures.

Table 2

Experiment	**Temperature / K**	**Rate constant / s^{-1}**
1	$T_1 = 303$	$k_1 = 1.55 \times 10^{-5}$
2	$T_2 = 333$	$k_2 = 1.70 \times 10^{-4}$

This equation can be used to calculate the activation energy, E_a

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

Calculate the value, in kJ mol^{-1}, of the activation energy, E_a

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

E_a ________________ kJ mol^{-1}

(5)

(h) Name and outline the mechanism for the reaction of butanone with KCN followed by dilute acid.

Name of mechanism ____

Outline of mechanism

(5)

(Total 21 marks)

Q3.

This question is about rates of reaction.
Iodine and propanone react together in an acid-catalysed reaction

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

A student completed a series of experiments to determine the order of reaction with respect to iodine.

Method

- Transfer 25 cm^3 of 1.0 mol dm^{-3} propanone solution into a conical flask.
- Add 10 cm^3 of 1.0 mol dm^{-3} HCl(aq)
- Add 25 cm^3 of 5.0×10^{-3} mol dm^{-3} I_2(aq) and start a timer.
- At intervals of 1 minute, remove a 1.0 cm^3 sample of the mixture and add each sample to a separate beaker containing an excess of $NaHCO_3$(aq)
- Titrate the contents of each beaker with a standard solution of sodium thiosulfate and record the volume of sodium thiosulfate used.

(a) Suggest why the 1.0 cm^3 portions of the reaction mixture are added to an excess of $NaHCO_3$ solution.

(2)

(b) Suggest why the order of this reaction with respect to propanone can be ignored in this experiment.

(2)

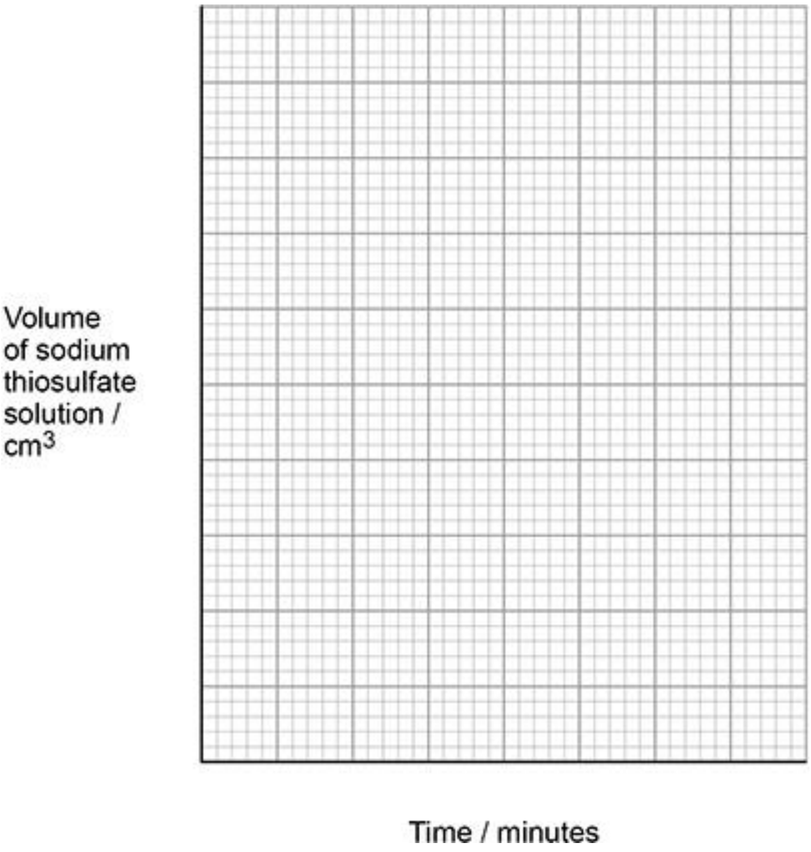
The volume of sodium thiosulfate solution used in each titration is proportional to the concentration of iodine in each beaker.

The table below shows the results of the experiment.

Time / minutes	**Volume of sodium thiosulfate solution / cm^3**
1	41
2	35
3	24
4	22
5	16
6	10

(c) Use the results in the table above to draw a graph of volume of sodium thiosulfate solution against time.

Draw a line of best fit.



(3)

(d) Explain how the graph shows that the reaction is zero-order with respect to iodine in the reaction between propanone and iodine.

____

____

____

____

____

____

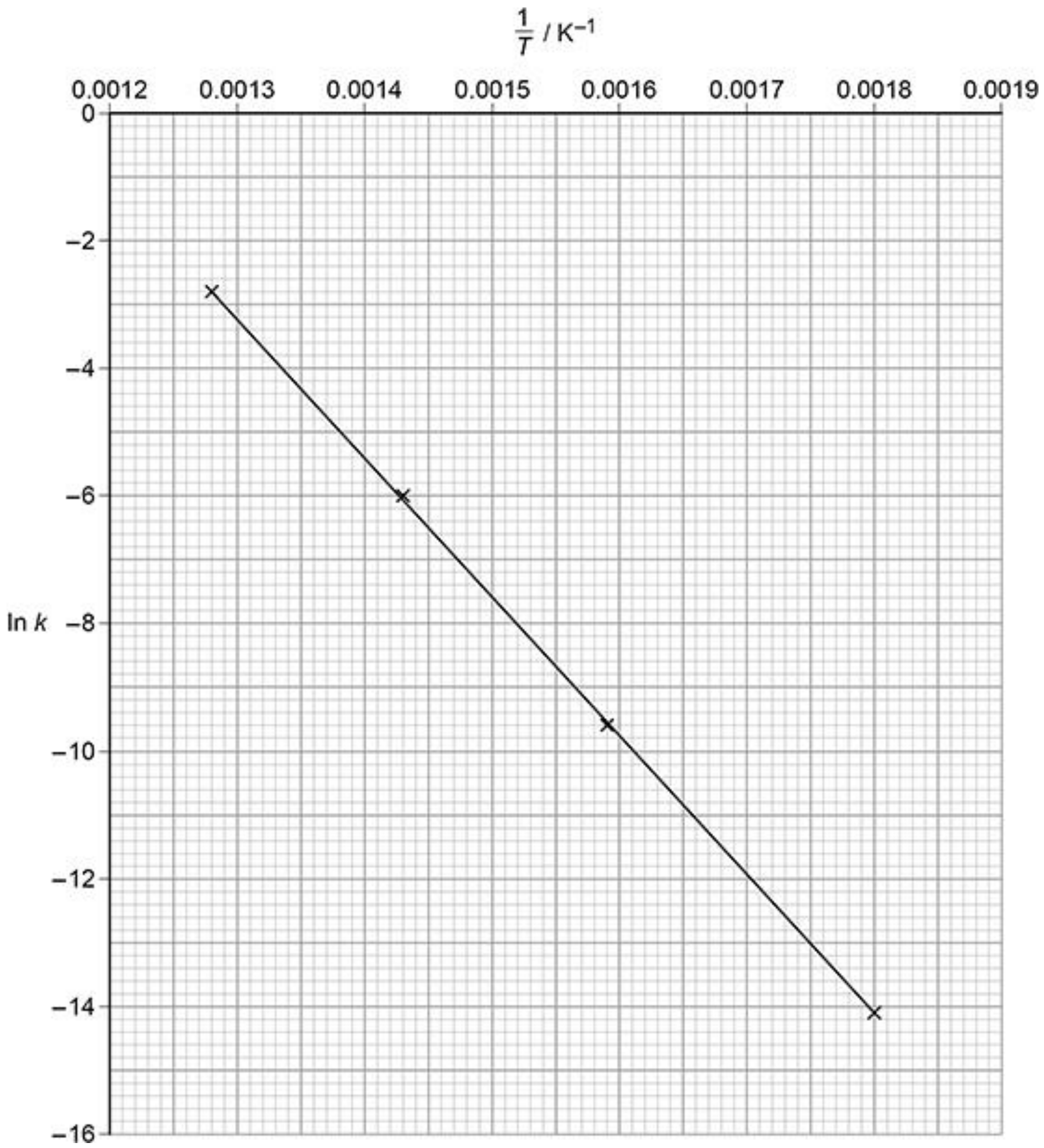
(2)

(e) The Arrhenius equation can be written as

$$\ln k = \frac{-E_a}{RT} + \ln A$$

The figure below shows a graph of ln k against $\frac{1}{T}$ for the reaction

$$2\,HI(g) \rightarrow H_2(g) + I_2(g)$$



Use the figure above to calculate a value for the activation energy (E_a), in kJ mol^{-1}, for this reaction.

The gas constant R = 8.31 J K^{-1} mol^{-1}

E_a ______________________ kJ mol^{-1}

(3)

(Total 12 marks)

Q4.

This question is about rates of reaction.

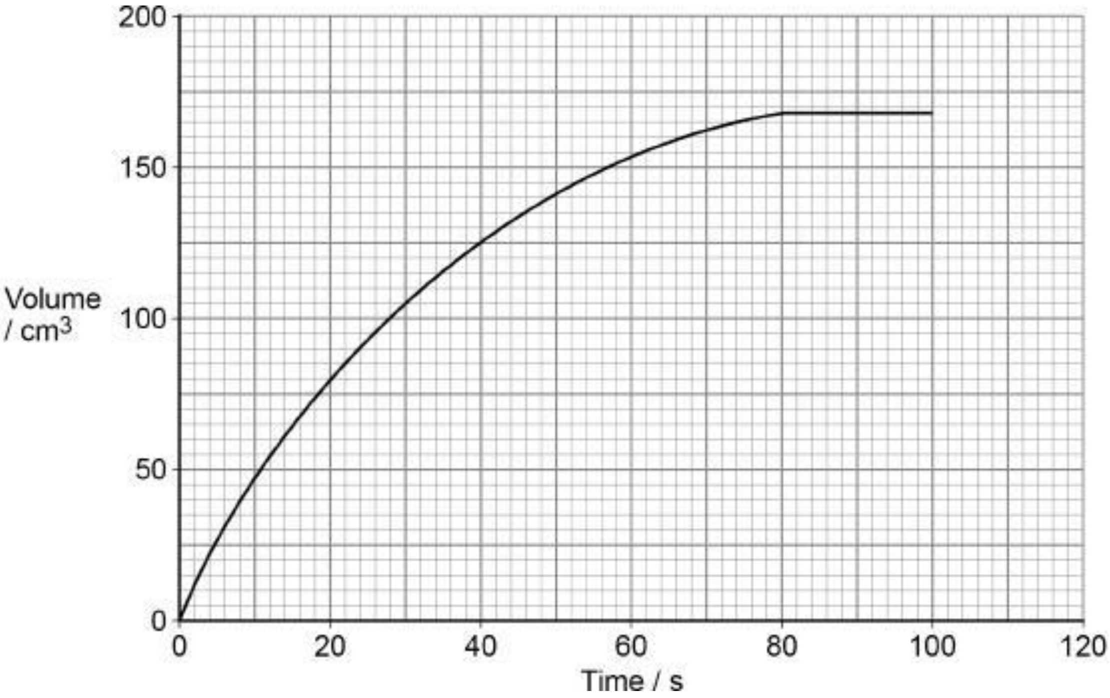
Phosphinate ions ($H_2PO_2^-$) react with hydroxide ions to produce hydrogen gas as shown.

$$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2$$

A student completed an experiment to determine the initial rate of this reaction.
The student used a solution containing phosphinate ions and measured the volume of hydrogen gas collected every 20 seconds at a constant temperature.

Figure 1 shows a graph of the student's results.

Figure 1



(a) Use the graph in **Figure 1** to determine the initial rate of reaction for this experiment. State its units. Show your working on the graph.

Rate ________________ Units ________________

(3)

(b) Another student reacted different initial concentrations of phosphinate ions with an excess of hydroxide ions. The student measured the time (*t*) taken to collect 15 cm^3 of hydrogen gas. Each experiment was carried out at the same temperature. The table shows the results.

Initial $[H_2PO_2^-]$ / mol dm^{-3}	***t* / s**
0.25	64
0.35	32
0.50	16
1.00	4

State the relationship between the initial concentration of phosphinate and time (*t*).

Deduce the order of the reaction with respect to phosphinate.

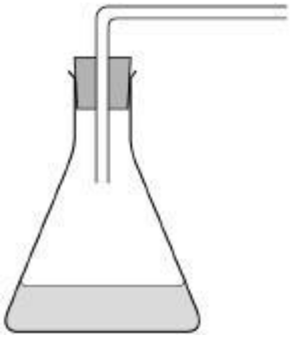
Relationship ____

Order ____

(2)

(c) Complete the diagram in **Figure 2** to show how the hydrogen gas could be collected and measured in the experiments in part (a) and (b).

Figure 2



The rate equation for a different reaction is

$$rate = k\,[L]\,[M]^2$$

(1)

(d) Deduce the overall effect on the rate of reaction when the concentrations of both **L** and **M** are halved.

____

____

____

(1)

(e) The rate of reaction is 0.0250 mol $dm^{-3}s^{-1}$ when the concentration of **L** is 0.0155 mol dm^{-3}

Calculate the concentration of **M** if the rate constant is 21.3 mol^{-2} dm^{6} s^{-1}

Concentration of **M** ________________ mol dm^{-3}

(3)

(f) Define the term overall order of reaction.

____

____

____

(1)

(Total 11 marks)

Q5.

Cisplatin, $[Pt(NH_3)_2Cl_2]$, is used as an anti-cancer drug.

(a) Cisplatin works by causing the death of rapidly dividing cells.

Name the process that is prevented by cisplatin during cell division.

____

(1)

After cisplatin enters a cell, one of the chloride ligands is replaced by a water molecule to form a complex ion, **B**.

(b) Give the equation for this reaction.

____

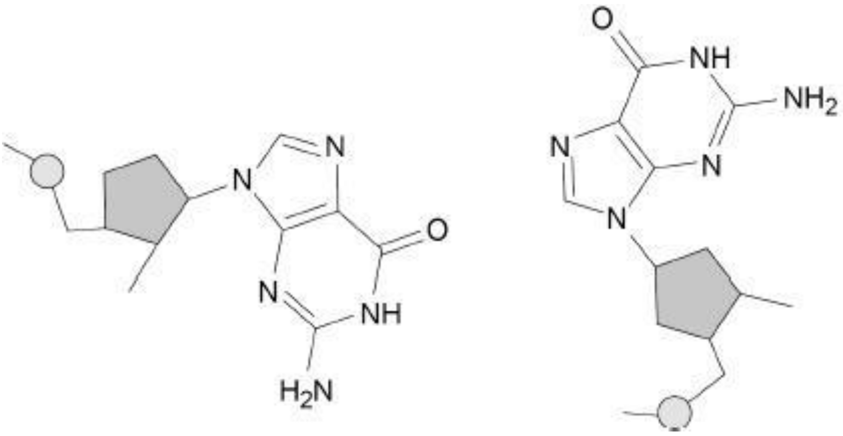
(2)

(c) When the complex ion **B** reacts with DNA, the water molecule is replaced as a bond forms between platinum and a nitrogen atom in a guanine nucleotide.
The remaining chloride ligand is also replaced as a bond forms between platinum and a nitrogen atom in another guanine nucleotide.

Figure 1 represents two adjacent guanine nucleotides in DNA.

Complete **figure 1** to show how the platinum complex forms a cross-link between the guanine nucleotides.

Figure 1



(2)

An experiment is done to investigate the rate of reaction in part (b).

(d) During the experiment the concentration of cisplatin is measured at one-minute intervals.

Explain how graphical methods can be used to process the measured results, to confirm that the reaction is first order.

(3)

In another experiment, the effect of temperature on the rate of the reaction in part (b) is investigated.

The table shows the results.

Temperature T / K	$\frac{1}{T}$ / K^{-1}	**Rate constant k / s^{-1}**	**ln k**
293	0.00341	1.97×10^{-8}	−17.7
303	0.00330	8.61×10^{-8}	−16.3
313	0.00319	3.43×10^{-7}	−14.9
318		6.63×10^{-7}	
323	0.00310	1.26×10^{-6}	−13.6

(e) Complete the table above.

(2)

(f) The Arrhenius equation can be written in the form

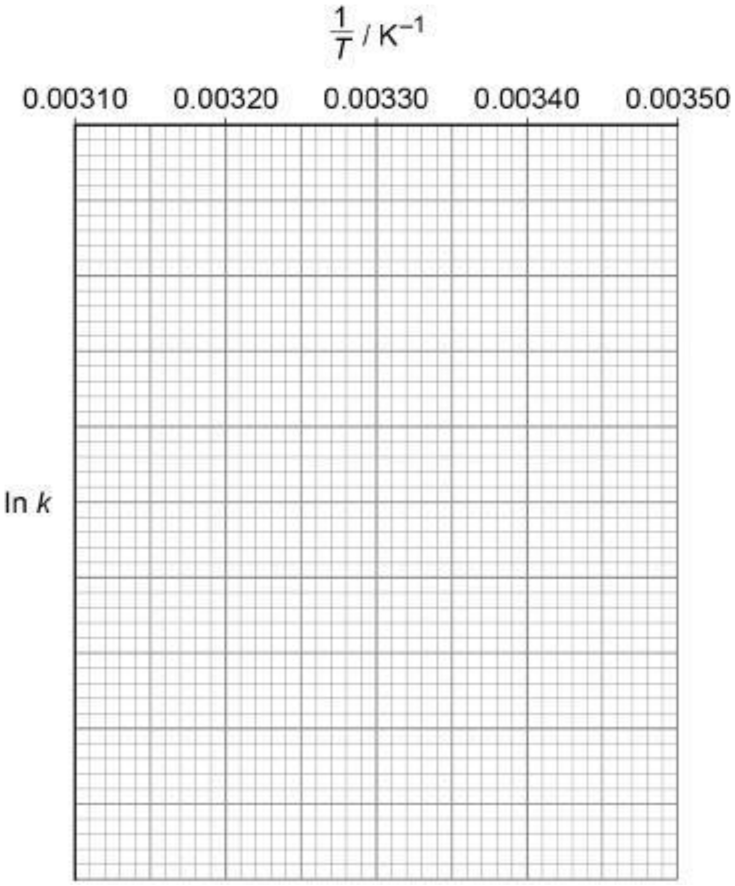
$$\ln k = \frac{-E_a}{RT} + \ln A$$

Use the data in the table above to plot a graph of ln k against $\frac{1}{T}$ on the grid in **Figure 2**.

Calculate the activation energy, E_a, in kJ mol^{-1}

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

Figure 2



E_a ________________ kJ mol^{-1}

(5)

(Total 15 marks)

Mark schemes

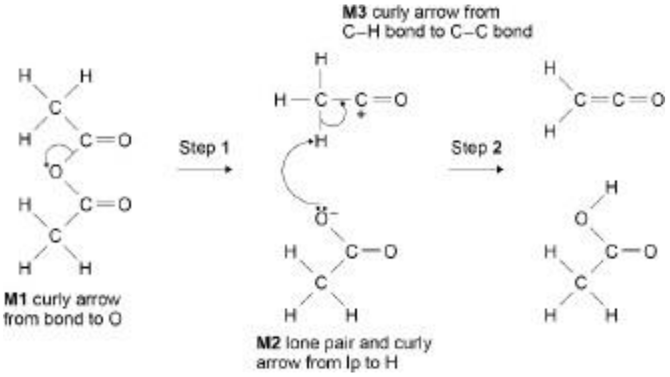
Q1.

(a) $C_nH_{2n-2}O$

Allow $C_nH_{2n}CO$ or $(CH_2)_nCO$ or $C_nH_{2(n-1)}O$

1

(b)



Allow other C-O bond breaking for M1

3

(c) M1 $\frac{k}{A} = e^{-Ea/RT}$

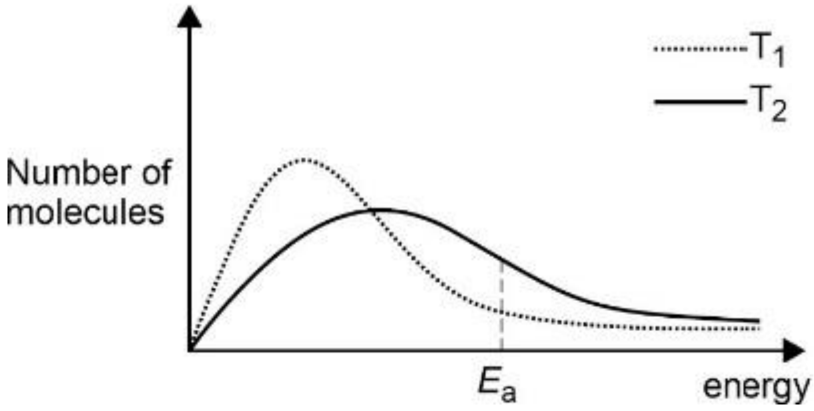
M2 $8.302 = \frac{34500}{8.31 \times T}$

M3 T = 500 K

OR via $\ln k = \ln A - \frac{Ea}{RT}$ *or shown with numbers*

3

(d)



M5 At T_2 (many) more particles have $E \geq E_a$

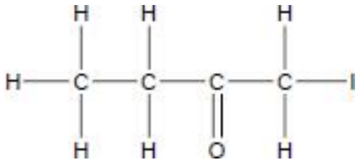
M1 x axis labelled correctly (kinetic not required)
AND y axis labelled correctly allow particles
M2 Ea labelled on x axis
M3 Distribution correct shape for T_1
M4 Peak at T_2 lower with max shifted right and only crosses once

5

[12]

Q2.

(a)



Apply list principle for more than one structure given

M1

1-iodobutan-2-one

Allow 1-iodo-2-butanone

M2

(b) $\frac{\text{Rate}}{[CH_3CH_2COCH_3][H^+]} = k$

Rearranged expression Or with numbers

M1

$k = 4.(04) \times 10^{-5}$ or 0.00004(04)

If upside down = 24752 mol dm^{-3} s

If multiply = 5.20 × 10^{-4} mol^{3} dm^{-9} s^{-}

M2

mol^{-1} dm^{3} s^{-1}

M3

(c) 3.6(25) × 10^{-5} (mol dm^{-3} s^{-1})

Allow 3.59 × 10^{-5} to 3.63 × 10^{-5}

1

(d) Brown colour removed

Goes colourless

Allow (orange) brown to colourless

Allow purple to colourless

1

(e) As T increases rate ($1/t$) increases OR time for completion decreases

M1

Exponentially
OR
By a greater/ increasing factor

Or rate increases more and more as temp increases ie description of exponential increase

M2

Many more particles have $E \geq E_a$

NOT just higher collision frequency

NOT just more successful collisions

M3

(f) Time = $\frac{1}{0.03}$ = 33 s

1

(g) $\ln(1.55 \times 10^{-5}/1.70 \times 10^{-4}) = \frac{E_a}{R}\left(\frac{1}{333} - \frac{1}{303}\right)$

Insertion of correct values

M1

$-2.39 = \frac{E_a}{R}(-2.97 \times 10^{-4})$

Evaluate LHS and fraction on RHS

M2

$\frac{2.39 \times 8.31}{2.97 \times 10^{-4}} = E_a$

Re-arrange for E_a

M3

66937

Evaluate

M4

66.9 kJ mol^{-1}

convert to kJ mol^{-1}

M5

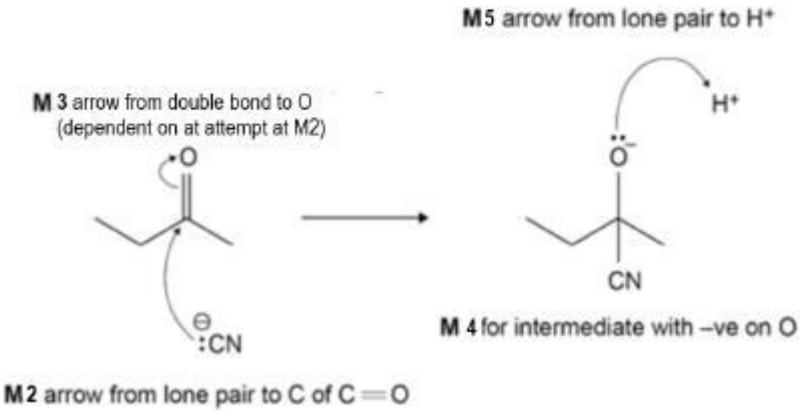
If only k_1 and k_2 reversed this gives a negative answer for E_a Lose M1 and M5

If AE in M2 allow ECF

Allow ECF from M4 to M5 for a correct unit conversion

Allow range 66.3 − 67.1

(h) Nucleophilic Addition



M1M2M3M4M5

ALLOW negative charge anywhere on cyanide

But attacking lone pair must be on C

Do not award M3 without attempt of M2

Allow M2 for attack to a positive carbon following breaking of C=O

Penalise covalent KCN in M2

M3 ignore partial charges unless wrong
Penalise M3 for incorrect connection between CN and C
NB Allow fully displayed or other structural formulae

[21]

Q3.

(a) The sodium hydrogencarbonate solution neutralises the acid (catalyst)

M1

So stops the reaction

M2

(b) The concentration/amount of propanone is much larger than/200 times larger than the concentration/amount of iodine

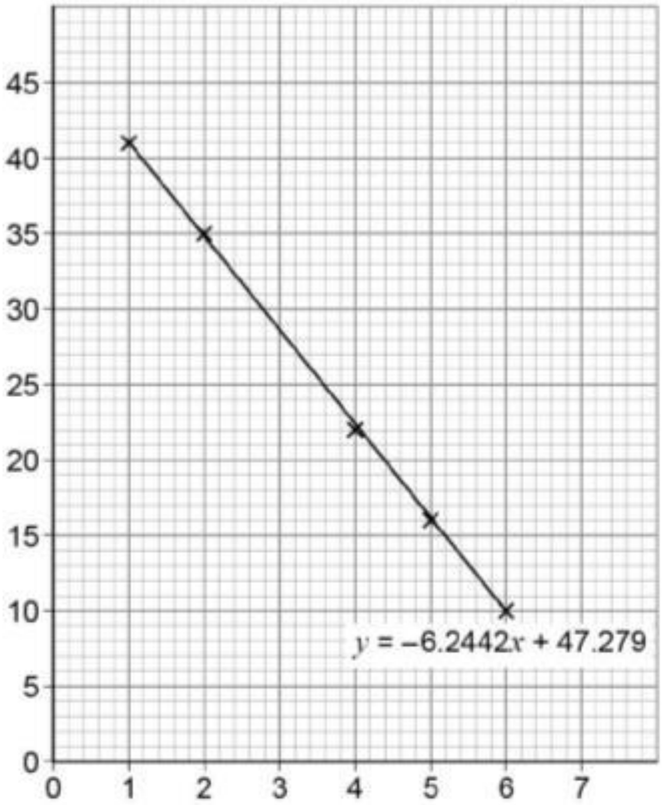
M1

Concentration of propanone is (almost) constant

The change in concentration in propanone is negligible

M2

(c)



M1

Suitable axes (plotted points must take up at least half of the grid)

M2

For all points correctly plotted to ± $^1/_2$ small square

For straight line of best fit which avoids the anomalous plot M1

M3

(d) The graph is a straight line / has a constant gradient

M1

So the rate of reaction does not change as the concentration (of iodine) changes / the iodine is being used up at a constant rate.

Correct rate vs conc graph scores M2

M2

(e) Gradient = (−14.1 − −2.8) / (0.00180 − 0.00128)
= −11.3 / 0.00052
= −21731

Allow -21330 to -22130

M1

Gradient = $-E_a$ / R
$-E_a$ = their answer x 8.31 (= 180583 J mol^{-1})

M2

E_a = M2 ÷ 1000 (= 181 kJ mol^{-1})

M3

[12]

Q4.

(a) **M1** tangent drawn to the curve at 0,0

If tangent not drawn at 0,0 then allow conseq gradient calculation

1

M2 Evidence of value used in calculation leading to initial rate = 5.5

Note allow 5 – 7

1

M3 $cm^3\ s^{-1}$

NOT cm^3 / s

1

(b) **M1** $[H_2PO_2^-]^2\ \alpha\ 1/t$

Accept time argument eg if conc doubled time is quartered

Accept suitable words that implies a square or square root relationship

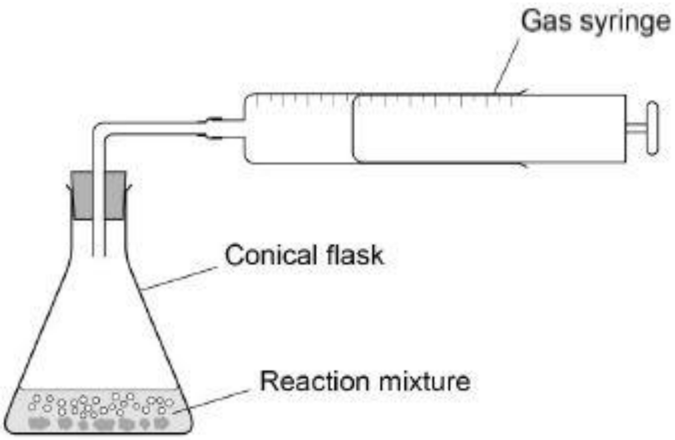
1

M2 Order = 2

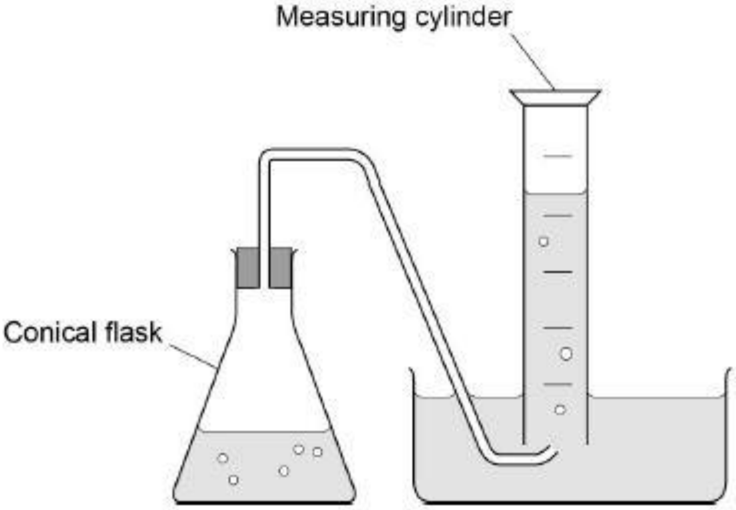
Not simple description of as conc increases time decreases 1

1

(c)



Either gas syringe or measuring cylinder over water



Tubing shown should not be closed
Syringe should have a plunger shown
Allow lack of graduations

1

(d) Falls by a factor of 8

OR Multiplied by $^{1}/8$

OR Divided by 8
Allow halved then quartered / Decreases by 2^3

1

(e) **M1** $[M]^2 = \underline{\text{Rate}}$

Re-arrangement

1

M2 $[M]^2 = \frac{0.0250}{21.3 \times 0.0155}$ (=7.57 × 10–2)

Inserts correct numbers into their rearranged expression

1

M3 $[M] = \sqrt{7.57 \times 10^{-2}} = 0.275$ mol dm^{-3} (min 2 sf)

Takes square root (allow ecf for square root of their M2)
Common error is to use 0.25 rather than 0.025. This leads to an

answer of 0.870. Scores 2

Upside-down expression leads to an answer of 3.63. Scores 2

1

(f) The sum of powers/indices (to which the concentrations are raised in the rate equation)

All the orders added/ sum of the (individual) orders

This can be explained using a general rate equation stated as an example

e.g. Rate = $k[A]^x[B]^y$ *and the overall order is* $x + y$

1

[11]

Q5.

(a) <u>DNA</u> Replication

NOT mitosis

NOT DNA synthesis

Ignore terms relating to cell division processes

Ignore ‘damages DNA’

Ignore DNA transcription

Ignore ’cell replication’

1

(b) $[Pt(NH_3)_2Cl_2] + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$

***M1** Correct formula **and** charge of B*

1

***M2** Correct balancing **and** charges in equation*

1

*Allow **M2** if the **only** error in complex B is the charge*

*(**M1** not awarded) with* Cl^- ***only***

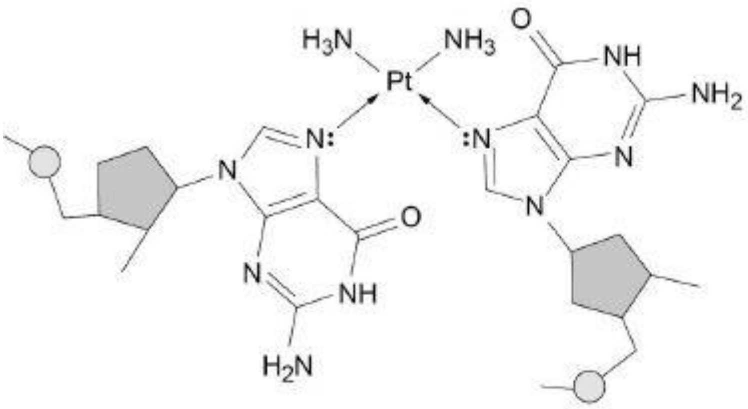
ALLOW complexes without [ ] and/or ( ) around H_2O

IGNORE ( ) around Cl

*NOT any additional different species (loses **M2**)*

(allow uncancelled water on both sides)

(c)



***M1** Pt in a cis-diammine complex bonded to the correct nitrogen atoms*

Pt must have the two ammonia ligands shown

NOT if drawn as trans

IGNORE any charge on Pt

Ignore any wedges and dashes (3D representations)

1

***M2** both lone pairs shown **OR** two arrows indicating co-ordinate bonds*

*Allow **M2** if bonds to platinum are from the incorrect nitrogen atoms*

1

(d) **M1** plot concentration (y-axis) against time (x-axis) **and** take tangents / (calculate the) gradients (to calculate rates)

Allow concentration-time graph

NOT time-concentration graph (unless clarified in words or sketch) but mark on

1

M2 Plot rate/gradients against conc

1

M3 straight line through origin / directly proportional confirms first order

allow first order if rate halves/doubles when conc halves/doubles

1

*Alternatives to **M2** and **M3**:*

***M2** Plot a graph of log rate vs log conc*
***M3** (Straight) line of gradient = 1*

***M2** measure (at least) two half-lives (in this case, tangents not required for M1)*
***M3** constant half-life means first order*

***M2** compare rates/gradients at different concentrations*
***M3** first order if rate halves when conc halves*

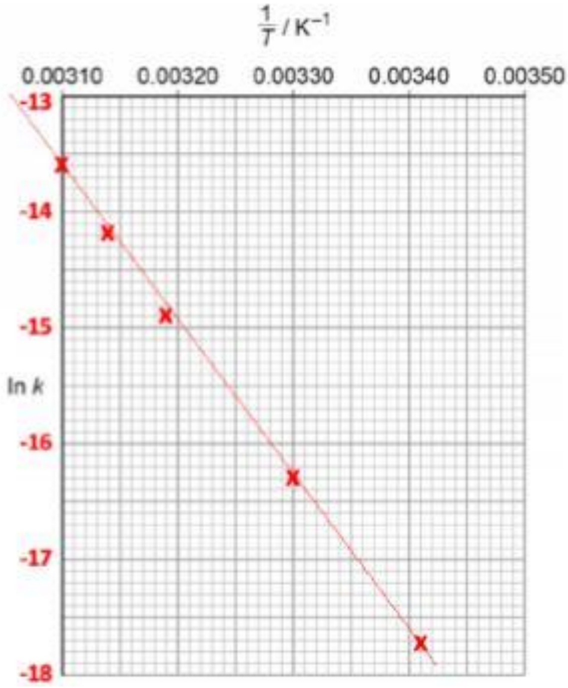
(e)

temperature, T / K	$\frac{1}{T}$ / K^{-1}	rate constant, k / s^{-1}	ln k
318	0.00314	6.63×10^{-7}	–14.2

Allow 3.14×10^{-3}

2

(f)



Gradient = −13 125

$\left(-13125 = \frac{-E_a}{R}\right)$

E_a = 13 125 x 8.31 = 109 069

= 109 (kJ mol^{-1})

Vertical axis with sensible scales (plotted points must take up more than half the grid) NOT M1 if y-axis in wrong direction

1

all points plotted correctly (within ±0.5 small square)

1

Best fit straight line based on the student's data (ignoring anomalous point if relevant)

1

Gradient calculated within range: 12876 - 13598

1

Mark is for their (gradient x 8.31) ***and*** *conversion into kJmol^{-1}*

E_a in the range: 107 – 114 kJ mol^{-1}

NOT a negative activation energy

1

[15]