

OCR A Chemistry A-Level
Module 5 - Physical Chemistry &
Transition Elements

Energetics
Notes and Example Calculations
Answers given at the end of the booklet





Rate of Reaction

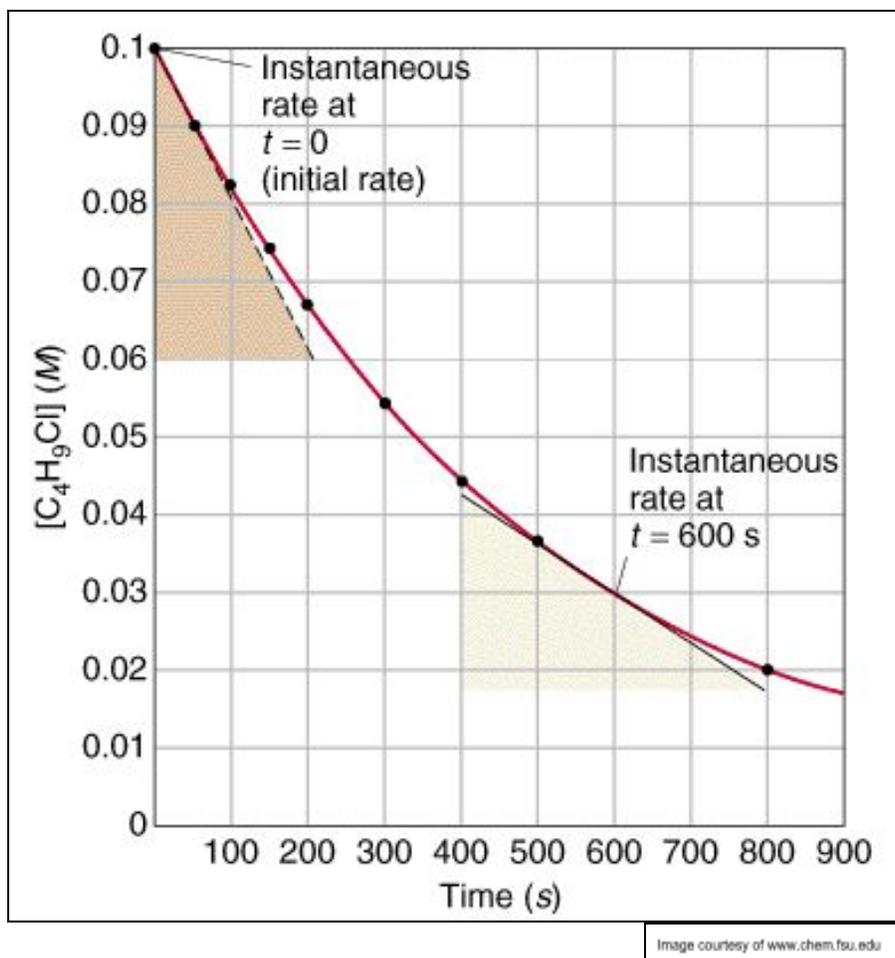
Rate of reaction is usually measured as the change in concentration of a reactant or product with time:

$$\text{Rate} = \frac{\text{change in concentration of reactant or product}}{\text{time for the change to take place}}$$

Unit = $\text{mol dm}^{-3} \text{ s}^{-1}$

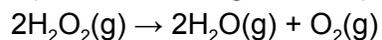
In order to calculate the rate of reaction from a concentration-time graph:

- Find the initial rate by drawing a tangent at $t=0$.
- Find rate at a certain time draw a tangent at that time on the graph.



Try this question...

1. Hydrogen peroxide, H_2O_2 , decomposes according to the equation:



In an experiment, the concentration of the reactant H_2O_2 was measured over a period of time. The results are shown below:

Time/s	0	15	30	60	100	180
$[\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	0.40	0.28	0.19	0.07	0.03	0.01

Plot a graph to show how concentration varies with time and use your graph to calculate the rate of reaction:

- Initially
- When $[\text{H}_2\text{O}_2] = 0.20 \text{ mol dm}^{-3}$
- When $[\text{H}_2\text{O}_2] = 0.10 \text{ mol dm}^{-3}$

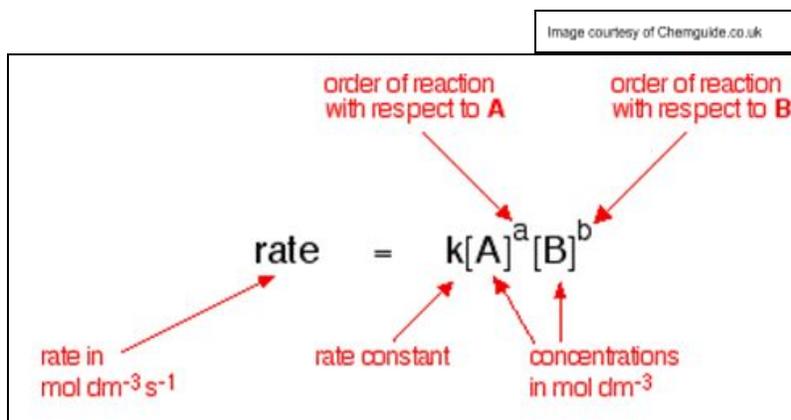




Orders of Reaction

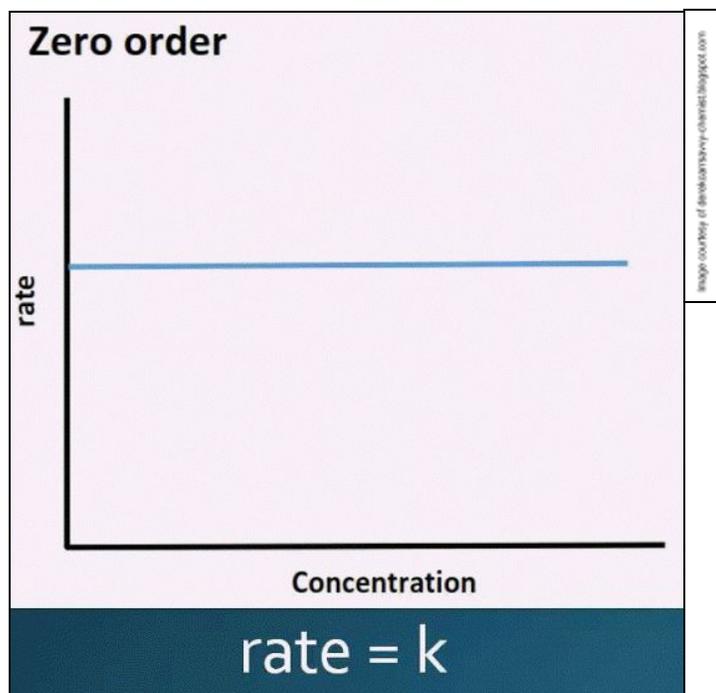
The order with respect to reactant is the power to which the concentration of the reactant is raised in the rate equation. The order of the reaction cannot be worked out from the overall equation. It only be worked out from experimental data by using a graphical method or initial rate method.

Example of a rate equation:



Zero order reaction

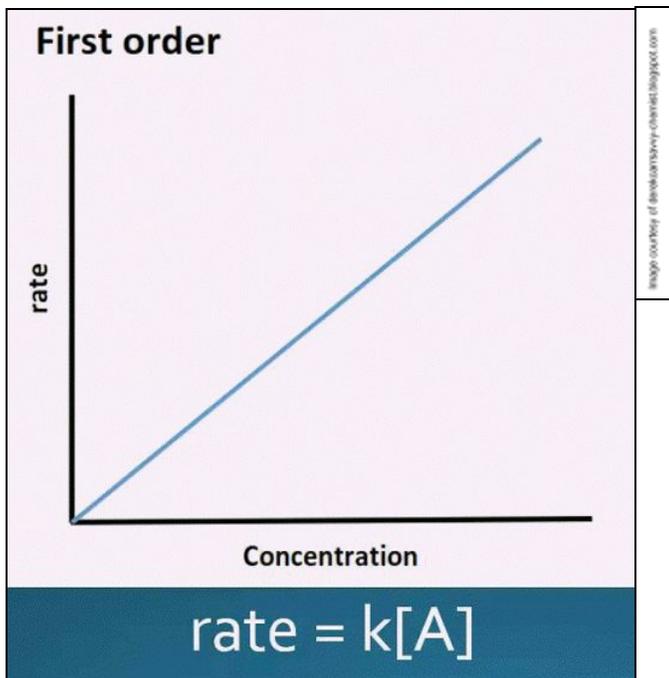
The concentration of the reactant has no effect on the reaction and therefore has no effect on the rate of the reaction.





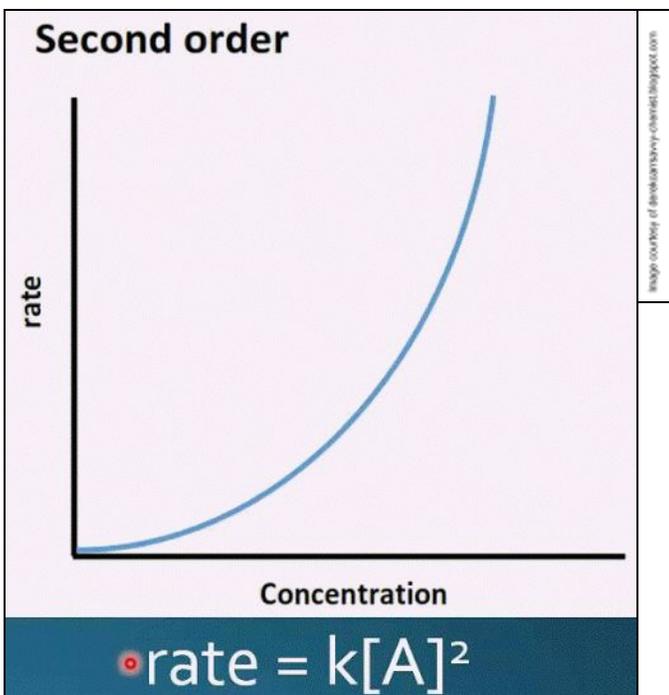
1st order reaction

The rate is directly proportional to the concentration. Therefore if the concentration of A doubles the rate doubles.



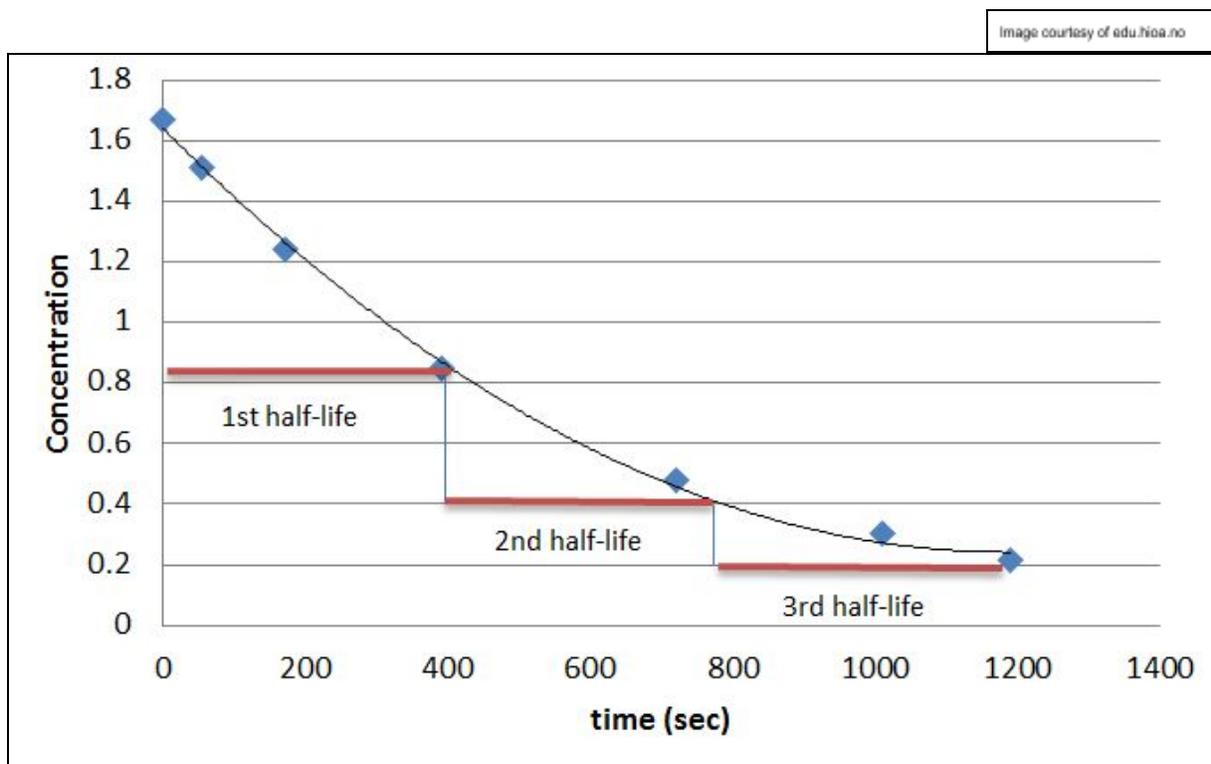
2nd order reaction

The rate is proportional to the square of the reactant. Therefore if the concentration of A doubles the rate quadruples.





The concentration-time graphs for 1st and 2nd order are similar so to distinguish between work out the half life of each graph. The graph with a constant half-life is 1st order of reaction.



Determining order of reaction, rate equation, rate constant and units using the initial rates method

Example 1:

The initial rates of the reaction $2A + B \rightarrow 2C + D$ at various concentrations of A and B are given below:

[A] mol dm ⁻³	[B] mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
0.01	0.20	0.10
0.02	0.20	0.20
0.01	0.40	0.40





a) What is the order of reaction with respect to A and B?

[Two data sets have to be compared, where for one substance the concentration stays the same and for the other it changes. This allows the effect, if any, on initial rate to be seen.]

Step 1: Find two sets of data where the concentration of B stays the same.

⇒ Experiment 1 and 2. [B] stays the same at 0.2 mol dm^{-3} , [A] doubles and the initial rate doubles.

Step 2: Deduce the order of reaction with respect to A.

⇒ When [A] doubles and the initial rate doubles meaning they are directly proportional.
⇒ It is **1st order of reaction**

Step 3: Find two sets of data where the concentration of A stays the same.

⇒ Experiment 1 and 3. [A] stays the same at 0.1 mol dm^{-3} , [B] doubles and the initial rate quadruples.

Step 4: Deduce the order of reaction with respect to B.

⇒ When [B] doubles and the initial rate quadruples meaning rate is proportional to the square of the concentration of the reactant.
⇒ It is **2nd order of reaction**

b) What is the overall order of reaction?

Step 1: Add the order of reaction with respect to all the reactants together to find out the overall order of reaction.

⇒ $1 + 2 = \underline{3}$

c) What is the value of the rate constant and its units?

Step 1: Write the rate equation.

⇒ Rate = $k[A][B]^2$





Step 2: Rearrange the equation so that the rate constant, k , is the subject.

$$\Rightarrow k = \text{rate} / [A][B]^2$$

Step 3: Input values from the table

$$\Rightarrow k = 0.1 / (0.01 \times (0.2^2))$$
$$= \underline{\underline{250}}$$

Step 4: Work out the unit of the rate constant by subbing the units into the equation.

$$\Rightarrow k = \frac{\text{rate}}{[A][B]^2}$$

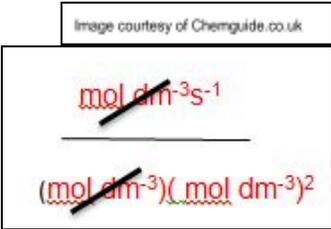
⇒ 

Image courtesy of Chemguide.co.uk

$$\Rightarrow \underline{\underline{\text{mol}^{-2}\text{dm}^6\text{s}^{-1}}}$$

d) What will be the rate of the reaction if the concentrations of A and B are both 0.01 mol dm^{-3} ?

Step 1: Use the rate equation and input the values to work out the rate of reaction.

$$\Rightarrow \text{Rate} = 250 \times (0.1) \times (0.1)^2$$
$$= 0.25 \text{ mol dm}^3 \text{ s}^{-1}$$





Example 2:

For the reaction $F_2(g) + ClO_2(g) \rightarrow 2FCIO_2(g)$, the following rate data were collected:

$[F_2]$ mol dm ⁻³	$[ClO_2]$ mol dm ⁻³	Initial rate mol dm ⁻³ s ⁻¹
0.10	0.01	1.2×10^{-3}
0.10	0.04	4.8×10^{-3}
0.20	0.01	2.4×10^{-3}

What is the rate constant for the reaction?

Step 1: Work out the order with respect to F_2 .

⇒ Experiment 1 and 2. $[F_2]$ doubles and the rate doubles.

⇒ 1st order with respect to F_2 .

Step 2: Work out the order with respect to ClO_2

⇒ Experiment 1 and 2. $[ClO_2]$ increases by 4 and the rate increases by 4.

⇒ 1st order with respect to ClO_2

Step 3: Write the rate equation.

⇒ Rate = $k[F_2][ClO_2]$

Step 4: Rearrange the rate equation to calculate the rate constant, k .

⇒ $k = \text{rate} / ([F_2][ClO_2])$

$$= \frac{1.2 \times 10^{-3}}{(0.1)(0.01)}$$

⇒ **$1.2 \text{ mol dm}^{-3} \text{ s}^{-1}$**



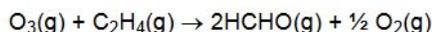


Worked Exam Style Question

Question 1

One cause of low-level smog is the reaction of ozone, O_3 , with ethene, C_2H_4 . The smog contains methanal, $HCHO(g)$.

The equation for methanal production is shown below.



The rate of the reaction was investigated, using a series of different concentrations of either $C_2H_4(g)$ or $O_3(g)$, by measuring the initial rate of formation of $HCHO(g)$.

The results are shown below.

experiment	$[O_3(g)]$ / $10^{-7} \text{ mol dm}^{-3}$	$[C_2H_4(g)]$ / $10^{-8} \text{ mol dm}^{-3}$	initial rate / $10^{-12} \text{ mol dm}^{-3} \text{ s}^{-1}$
1	0.5	1.0	1.0
2	2.0	1.0	4.0
3	4.0	2.0	16.0

[3 marks]

Step 1:
the

with O_3 .
(i) Analyse and interpret the results to deduce the order of reaction of each reactant and the rate equation.

Work out
order of
reaction
respect to

⇒ Experiment 1 and 2. $[O_3]$ increases by 4 and the rate increases by 4.
⇒ 1st order with respect to O_3 .

Step 2: Work out the order of reaction with respect to C_2H_4 .

⇒ Note there are **not** 2 sets of data with the same concentration of O_3 . However experiments 2 and 3 can be used as the order of reaction of O_3 is known.

⇒ Using experiment 2 and 3, the $[C_2H_4]$ increases by 2 and the rate increases by 2 therefore it is 1st order with respect to C_2H_4 .

Note:

As the order for O_3 is known to be 1st order of reaction in between experiment 2 and 3 the concentration doubles therefore the rate also doubles.

Therefore the new rate is 8×10^{-12} , you can use this value to compare the effect on the rate the concentration of C_2H_4 has.

The initial rate doubled (8×10^{-12} to 16×10^{-12}) just as the concentration of C_2H_4 did.





⇒ 1st order of reaction.

Step 3: Write the rate equation.

$$\Rightarrow \text{Rate} = k[\text{O}_3][\text{C}_2\text{H}_4]$$

Try these questions...

2.

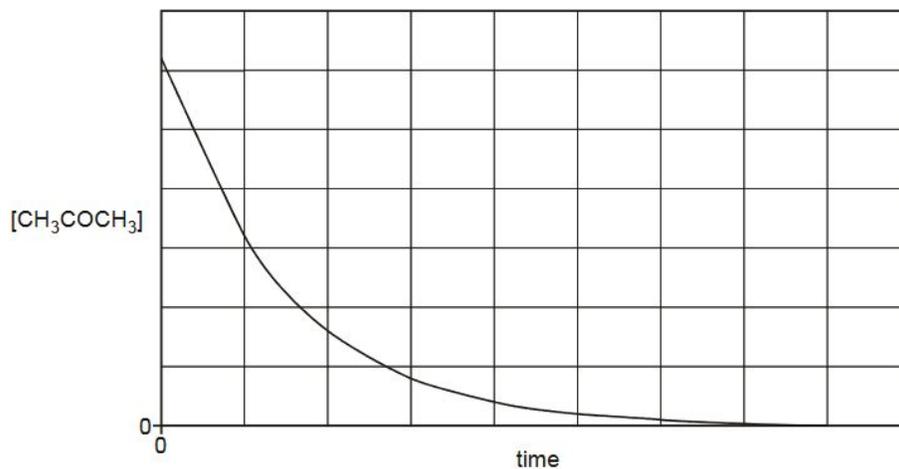
In this question, one mark is available for the quality of use and organisation of scientific terms.

Propanone reacts with iodine in the presence of dilute hydrochloric acid.

A student carried out an investigation into the kinetics of this reaction.

He measured how the concentration of propanone changes with time. He also investigated how different concentrations of iodine and hydrochloric acid affect the initial rate of the reaction.

The graph and results are shown below.

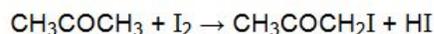


$[\text{CH}_3\text{COCH}_3]$ / mol dm^{-3}	$[\text{I}_2]$ / mol dm^{-3}	$[\text{H}^+]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1.5×10^{-3}	0.0300	0.0200	2.1×10^{-9}
1.5×10^{-3}	0.0300	0.0400	4.2×10^{-9}
1.5×10^{-3}	0.0600	0.0400	4.2×10^{-9}





The overall equation for the reaction is given below.

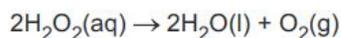


This is a multi-step reaction.

- What conclusions can be drawn about the kinetics of this reaction from the student's investigation? Justify your reasoning.
- Calculate the rate constant for this reaction, including units.

3.

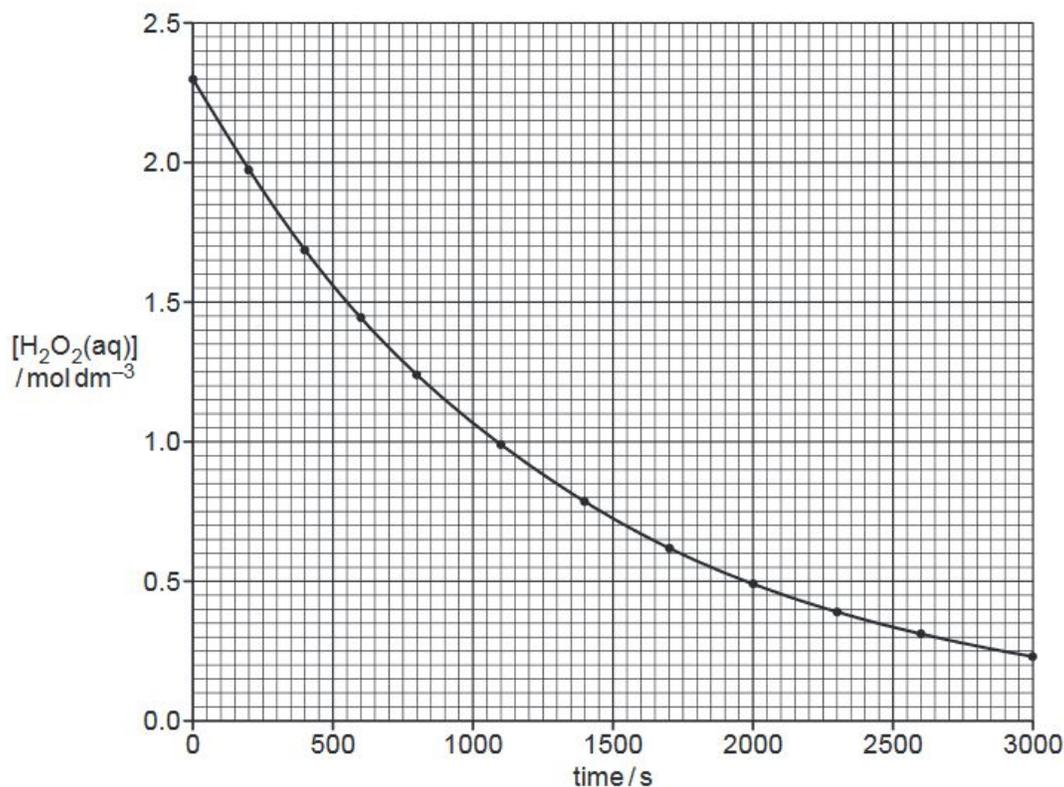
Aqueous solutions of hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, decompose as in the equation below.



A student investigates the decomposition of $\text{H}_2\text{O}_2(\text{aq})$ by measuring the volume of oxygen gas produced over time. All gas volumes are measured at room temperature and pressure.

The student uses 25.0 cm^3 of 2.30 mol dm^{-3} H_2O_2 .

From the results, the student determines the concentration of $\text{H}_2\text{O}_2(\text{aq})$ at each time. The student then plots a concentration–time graph.



(c)* Determine the initial rate of reaction, the order with respect to H_2O_2 , and the rate constant.

[6 marks]





Arrhenius Equation

The Arrhenius equation can be used to work out the activation energy of a system.

Image courtesy of SlidePlayer

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = -\frac{E_a}{RT} + \ln A$$

Where:

k	=	Chemical Reaction Rate
A	=	Pre-exponential Factor
E_a	=	Activation Energy
R	=	Gas Constant
T	=	Temperature in Kelvin

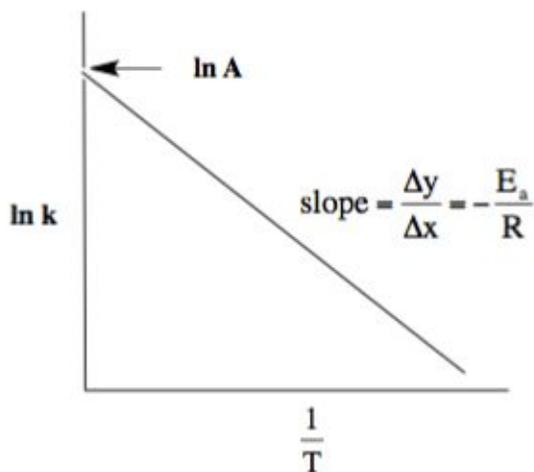
Units:

k - $\text{mol dm}^{-3}\text{s}^{-1}$

E_a - Joules (J)

T - Kelvin (K)

Activation energy can be found using a graph :



$$\ln(k) = \left[\frac{-E_a}{R} \right] \left[\frac{1}{T} \right] + \ln(A)$$

$$y = mx + b$$

1. Work out the gradient (this value = $-E_a / R$)
2. Multiply this value by the negative gas constant (-8.314)

The y-intercept - $\ln(A)$ can also be found from this graph.

$C = \ln(A)$





$$e^C = A$$

Example 1:

The rate constant for the reaction between Ca and HCl was measured at different temperatures. The results obtained were:

T(K)	290	310	330	350
k (mol dm ⁻³ s ⁻¹)	0.0030	0.0216	0.122	0.567

Use the Arrhenius equation to calculate the pre-exponential factor at 290K if the activation energy was 55.5 kJmol⁻¹.

Step 1: Decide which form of the Arrhenius equation would be easier to use and rearrange so that the pre-exponential factor, A, is the subject.

⇒ In this case you should use $k = Ae^{-E_a/RT}$

$$A = \frac{k}{e^{-E_a/RT}}$$

Step 2: Input values into the equation to work out the value of the pre-exponential factor.

$$A = \frac{0.003}{e^{-55500 / 8.314 \times 290}}$$

$$= \underline{2.98 \times 10^7} \quad (3 \text{ s.f.})$$

Example 2:

Calculate E_a of a reaction at 330 K and a rate constant $1.3 \times 10^{-4} \text{ s}^{-1}$. Assume $A = 4.55 \times 10^{13}$ and $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$.

Step 1: Decide which form of the Arrhenius equation would be the easiest to use and rearrange the equation so that activation energy is the subject.

⇒ In this case it is best to use $\ln k = \frac{-E_a}{RT} + \ln A$

$$\Rightarrow E_a = (\ln(K) - \ln(A)) \times -RT$$





Step 2: Input the values into the equation

$$E_a = \ln(1.3 \times 10^{-4}) - \ln(4.55 \times 10^{13}) \times (-8.314 \times 330) = 110833 \text{ J}$$

⇒ 111 kJ

Try this question...

4.

(ii) The rate constant, k , for this reaction is determined at different temperatures, T .

Explain how the student could determine the activation energy, E_a , for the reaction graphically using values of k and T .

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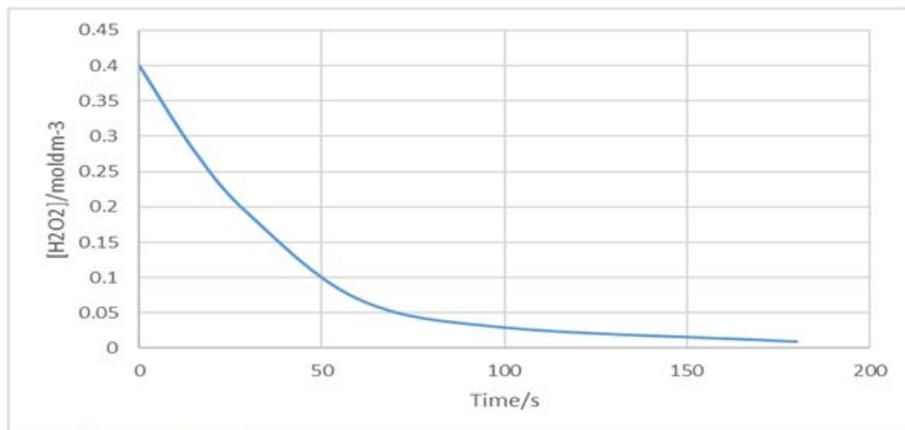
..... [3]





Answers

Q1.



- a) $(0.40 - 0.20) / 20 = 0.010 \text{ mol dm}^{-3}\text{s}^{-1}$
b) $(0.288 - 0.114) / 30 = 0.0058 \text{ mol dm}^{-3}\text{s}^{-1}$
c) $(0.134 - 0.036) / 30 = 0.0033 \text{ mol dm}^{-3}\text{s}^{-1}$

Q2.

From graph, constant half-life (1)

Therefore 1st order w.r.t. [CH₃COCH₃] (1)

2

From table, rate doubles when [H⁺] doubles (1)

Therefore 1st order w.r.t. [H⁺] (1)

2

From table, rate stays same when [I₂] doubles (1)

Therefore zero order w.r.t. [I₂] (1)

Order with no justification does **not** score.

2

rate = $k[\text{H}^+][\text{CH}_3\text{COCH}_3]$ (1)

(from all three pieces of evidence)

$$k = \frac{\text{rate}}{[\text{H}^+][\text{CH}_3\text{COCH}_3]} = \frac{2.1 \times 10^{-9}}{0.02 \times 1.5 \times 10^{-3}} \quad (1)$$

$$= 7.0 \times 10^{-5} \text{ (1) dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (1)}$$

accept 7×10^{-5}

4



Q3

Answer	Marks	Guidance
<p>Please refer to the marking instructions on page 5 of mark scheme for guidance on marking this question.</p> <p>Level 3 (5–6 marks) A comprehensive conclusion using quantitative data from the graph to correctly determine initial rate AND half lives/gradient with 1st order conclusion for H₂O₂ AND determination of k.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured.</i> Clear working for initial rate, half life/gradient and order and k. Units mostly correct throughout.</p> <p>Level 2 (3–4 marks) Attempts to describe all three scientific points but explanations may be incomplete. OR Explains two scientific points thoroughly with few omissions.</p> <p><i>There is a line of reasoning with some structure and supported by some evidence. The scientific points are supported by evidence from the graph.</i></p> <p>Level 1 (1–2 marks) Reaches a simple conclusion using at least one piece of quantitative data from the graph. Attempts to calculate initial rate OR half life.</p> <p><i>There is an attempt at a logical structure with a reasoned conclusion from the evidence.</i></p> <p>0 marks No response worthy of credit.</p>	6	<p>Indicative scientific points may include:</p> <p>Initial rate</p> <ul style="list-style-type: none"> Tangent shown on graph as line at t = 0 s Gradient determined in range: $1.5 - 2.0 \times 10^{-3}$ e.g. $\frac{2.3}{1300} = 1.77 \times 10^{-3}$ initial rate as gradient value with units: mol dm⁻³ s⁻¹ <p><i>For other methods contact TL</i></p> <p>Evidence for 1st order 2 methods</p> <ul style="list-style-type: none"> 1st order clearly linked to half-life OR 2 gradients: <p>1. Half life</p> <ul style="list-style-type: none"> Half life shown on graph Half life range 800–1000 s Two 'constant' half lives ± 50 s <p>2. Two gradients → two rates</p> <ul style="list-style-type: none"> 2 tangents shown on graph at c and c/2 Gradient at c/2 is half gradient at c e.g. c = 2.3 mol dm⁻³, gradient = 1.6×10^{-3} AND c = 1.15 mol dm⁻³, gradient = 0.8×10^{-3} <ul style="list-style-type: none"> For chosen method, conclusion: H₂O₂ is 1st order <p>Determination of k 2 methods</p> <ul style="list-style-type: none"> k clearly linked to rate OR half-life: <p>$k = \frac{\text{rate}}{[\text{H}_2\text{O}_2]}$ e.g. $k = \frac{1.6 \times 10^{-3}}{2.3} = 7 \times 10^{-4} \text{ s}^{-1}$</p> <p>OR $k = \frac{\ln 2}{t_{1/2}}$ e.g. $k = \frac{0.693}{950} = 7.3 \times 10^{-4} \text{ s}^{-1}$</p>

Q4.

Plot graph using $\ln k$ AND $1/T$ ✓ (Measure) gradient ✓ Independent mark $E_a = (-)R \times \text{gradient}$ OR $(-)8.314 \times \text{gradient}$ ✓ <ul style="list-style-type: none"> Independent mark, even if variables for graph are incorrect Subsumes 'gradient' mark 	3	<p>Unless otherwise stated, assume, that $\ln k$ is on y axis and $1/T$ is on x axis</p> <p>IGNORE intercept</p> <p>ALLOW gradient = $(-)\frac{E_a}{R}$</p> <hr/> <p>NOTE: ALLOW 'inverse graph' (special case)</p> <p>Plot graph of $1/T$ against $\ln k$ ✓</p> <p>(Measure) gradient ✓ Independent mark</p> <p>$E_a = (-)\frac{R}{\text{gradient}}$ OR $(-)\frac{8.314}{\text{gradient}}$</p> <p>OR gradient = $(-)\frac{R}{E_a}$ ✓ Subsumes 'gradient' mark</p>
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