A Standard Kinetics Question

A Level

The rate at which A and B react is given by the rate equation:

$$rate = k[\mathrm{A}]^n[\mathrm{B}]^m$$

where k is the rate constant.

Part A Order with respect to [B]

When $[\mathrm{A}]$ is constant, the initial reaction rate varies with $[\mathrm{B}]$ as shown below.

What is the value of m?

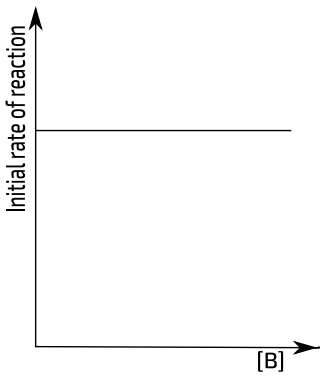

Figure 1: Graph showing initial rate of reaction with varying [B]

Part B Order with respect to [A]

The table below shows the initial value of $[A]$, and two values at later times, with $[B]$ remaining constant throughout.

Time / seconds	$[A]$ / $\mathrm{mol, dm^{-3}}$
0	0.100
300	0.050
600	0.025

How does the half-life of the concentration of A behave?

- More information is required
- It increases through time
- It decreases through time
- It is constant through time

Part C Value of n

Hence, what is the value of n?

Part D Effect of Temperature

The value of k, the rate constant for the reaction taking place at constant temperature was determined to be $3.1 \times 10^{-3}\ \mathrm{s^{-1}}$. How would you expect the value of k to change when the experiment was repeated at a lower temperature?

- It would stay the same
- It would increase
- It depends on the type of reaction
- It would decrease

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Ceriously Cringeworthy

A Level

C C C

Cr and Ce undergo the following redox reaction:

$$\mathrm{Cr(III)} + 3\,\mathrm{Ce(IV)} \longrightarrow \mathrm{Cr(VI)} + 3\,\mathrm{Ce(III)}$$

The rate of this reaction varies as follows:

$[\mathrm{Cr(III)}]\ /\mathrm{mol,dm^{-3}}$	$[\mathrm{Ce(IV)}]\ /\mathrm{mol,dm^{-3}}$	$[\mathrm{Cr(VI)}]\ /\mathrm{mol,dm^{-3}}$	$[\mathrm{Ce(III)}]\ /\mathrm{mol,dm^{-3}}$	$\mathrm{Rate}\ /\mathrm{mol,dm^{-3},s^{-1}}$
0.050	0.020	0.040	0.025	1.0×10^{-6}
0.100	0.020	0.040	0.025	2.0×10^{-6}
0.050	0.040	0.040	0.025	4.0×10^{-6}
0.050	0.020	0.020	0.025	1.0×10^{-6}
0.050	0.020	0.020	0.050	5.0×10^{-7}

Part A Partial reaction orders

What are the partial reaction orders with respect to $\mathrm{Cr(III)}$, $\mathrm{Ce(IV)}$, $\mathrm{Cr(VI)}$ and $\mathrm{Ce(III)}$?

- $1, 2, 0, 0$
- $1, 1, 0, 0$
- $1, 2, 0, -1$
- $1, 3, 0, 0$
- $1, 3, -1, -3$

Part B Overall order of reaction

What is the overall reaction order?

Part C Rate constant

Calculate the rate constant for the reaction.

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Graphing Concentration and Time

A Level

The decomposition of dinitrogen pentaoxide according to the equation

$$\mathrm{N_2O_5} \longrightarrow 2\,\mathrm{NO_2} + \frac{1}{2}\mathrm{O_2}$$

was studied as follows.

Using a solution of dinitrogen pentaoxide in tetrachloromethane the concentration of the oxide, $\mathrm{N_2O_5}$, remaining at various times during the decomposition was measured at a temperature of $318\,\mathrm{K}$. We use the notation $b = [\mathrm{N_2O_5}]$.

t / min	b / mol dm^{-3}
0	3.0
10	2.0
20	1.4
30	0.95
40	0.63
50	0.42
60	0.29
70	0.19

Part A Concentration time graph

Plot a graph of the concentration of N_2O_5 against time, and from this determine the time taken for the concentration to fall to half its original value.

And to fall to a quarter of its original value?

And to an eighth?

Part B Order of reaction

From these values, what is the order of this reaction?

Part C Rate equation

Now you know the order of reaction, what is the rate equation for this reaction? Use r to denote the rate, k to denote the rate constant, and b to denote the concentration of $\mathrm{N_2O_5}$.

The following symbols may be useful: `b, k, r`

Part D Rate constant

What is the value of the rate constant, k, at this temperature?

Part E Effect of temperature

If the reaction was carried out at a constant temperature greater than $318\,\mathrm{K}$, how would the rate constant change?

- It would increase.
- It would decrease.
- It depends on whether this is an exothermic or endothermic reaction.
- It would stay the same.

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Peroxide Puzzle

A Level

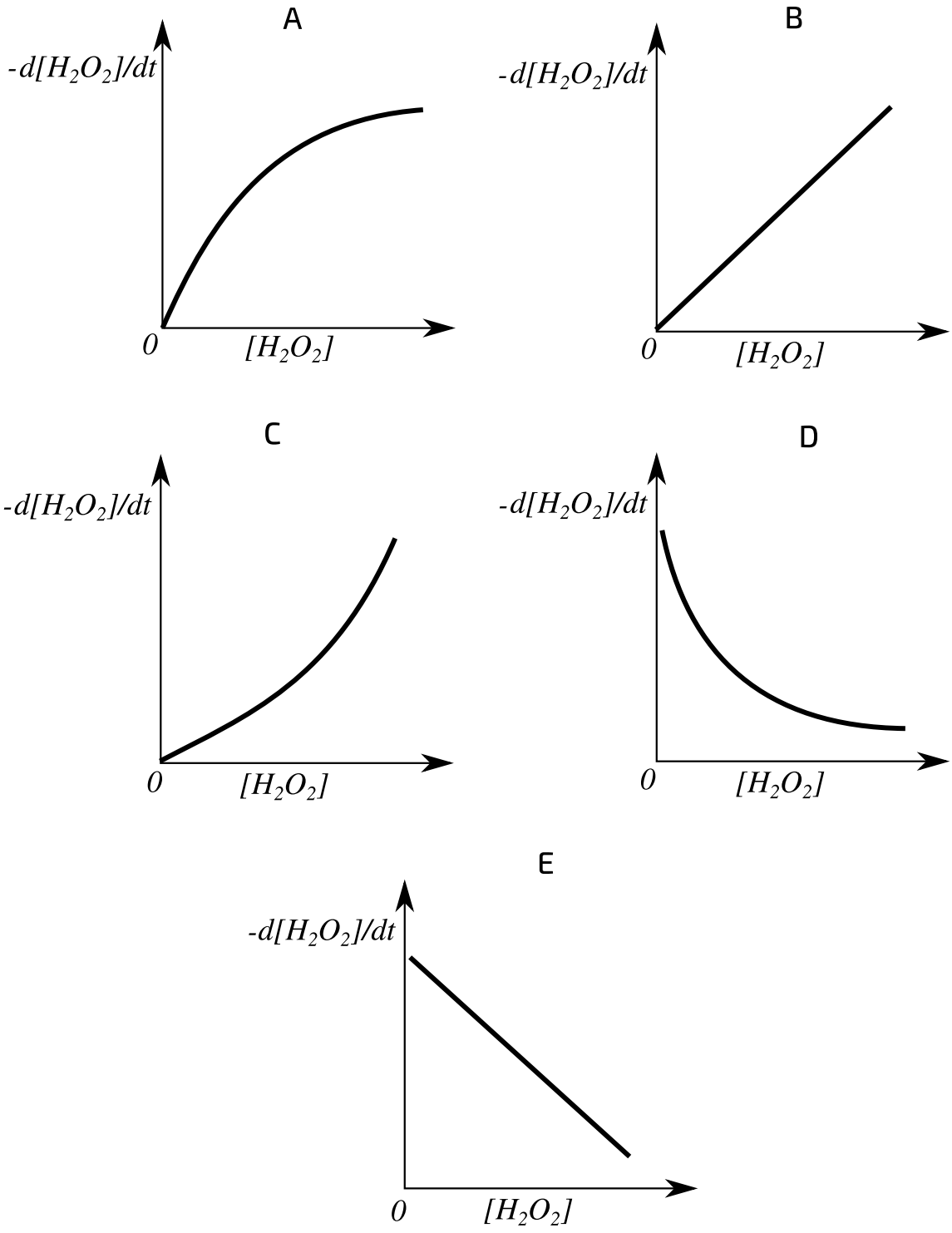

Figure 1: Graphs showing the rate of decomposition of hydrogen peroxide as a function of the concentration of hydrogen peroxide.

Which one of the graphs above would confirm that the decomposition of hydrogen peroxide was first order with respect to the concentration of hydrogen peroxide?

- A

- B
- C
- D
- E

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Concentration and Rate

A Level

The following data were obtained for the reaction between KOH and $CH_3COOCH_2CH_3$ (its IUPAC name is ethyl ethanoate, but it is more commonly called ethyl acetate) in water at $50\,^{\circ}C$.

Experiment number	Initial concentration of KOH/ $mol\,dm^{-3}$	Initial concentration of ethyl acetate/ $mol\,dm^{-3}$	Initial rate/ $mol\,dm^{-3}\,min^{-1}$
1	0.05	0.10	0.04
2	0.10	0.10	0.08
3	0.20	0.10	0.16
4	0.20	0.20	0.32
5	0.20	0.20	?

Part A Balanced equation

Write the simplest balanced equation for this reaction, using molecular formula. State symbols are not required.

Part B Order of reaction

What is the order of reaction with respect to KOH?

What is the order of reaction with respect to ethyl acetate, $CH_3COOCH_2CH_3$?

Hence, what is the overall order of this reaction?

Part C Rate equation

Write the rate equation for this reaction, using A to denote the concentration of KOH, B to denote the concentration of $\mathrm{CH_3COOCH_2CH_3}$, k to denote the rate constant, and r to denote the rate.

The following symbols may be useful: `A, B, k, r`

Part D Rate constant

Now, using the above equation, and the given data, calculate the rate constant.

Part E Determining the initial rate

Predict the initial rate of experiment 5.

Part F Effect of temperature

If the experiments were instead carried out at $30\,^{\circ}\mathrm{C}$, how would the rates change?

- The rates would decrease.
- The rates would stay the same.
- We need to know if this is an exothermic or endothermic reaction before predicting this.
- The rates of some of the experiments would increase, while the rates of the other experiments would decrease.
- The rates would increase.

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Initial Rates

A Level

In an investigation to determine the order of reaction with respect to various reactants, the initial concentrations of the reactants were varied, and then the experiment was repeated. The reaction investigated was

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \longrightarrow \mathrm{D}$$

A table of the results is given below. The rate constant at this temperature, k, was determined to be $0.100\,\mathrm{mol^{-2}\,dm^{6}\,s^{-1}}$ beforehand.

Experiment number	Initial concentration of A/$\mathrm{mol\,dm^{-3}}$	Initial concentration of B/$\mathrm{mol\,dm^{-3}}$	Initial concentration of C/$\mathrm{mol\,dm^{-3}}$	Initial rate/ $\mathrm{mol\,dm^{-3}\,s^{-1}}$
1	0.900	1.80	0.100	3.24
2	1.20	0.900	0.100	0.810
3	0.600	1.80	0.200	6.48
4	0.300	0.200	0.300	?

Part A Order with respect to A

What is the order of reaction with respect to A?

Part B Order with respect to B

With respect to B?

Part C Order with respect to C

And with respect to C?

Part D Initial rate

Predict the initial rate of experiment 4.

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Short Kinetics Question

A Level

The equation for alkaline hydrolysis of methyl ethanoate (commonly called methyl acetate) is given below.

$$CH_3COOCH_3 + OH^- \longrightarrow CH_3COO^- + CH_3OH$$

This reaction was carried out under conditions in which the initial concentrations of the ester and the hydroxide ion were the same and the following observations were recorded

Time / min	**Concentration of** OH^- **/** $\mathrm{mol\,dm^{-3}}$
0	10.0
3	7.4
5	6.3
7	5.5
10	4.6
15	3.6
21	2.9
25	2.5

Part A Order of reaction

Using a graphical method, determine the kinetic order of this reaction.

Part B Concentration of ester after 3 minutes

What was the remaining concentration of the ester after 3 minutes?

Part C Concentration of ester after 25 minutes

And what was the remaining concentration of the ester after 25 minutes?

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Rate Constant Units

Further A

P P P

The following questions are about rate constants of different equations and their units.

Part A A general reaction

The following reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$$

Has the rate law $r = k[A][B]$, where $[A]$ and $[B]$ denote the concentrations of A and B respectively, and r denotes the rate of reaction, measured in $\mathrm{mol\,dm^{-3}\,s^{-1}}$.

If the concentrations are measured in $\mathrm{mol\,dm^{-3}}$, what are the units of the rate constant, k? Give your answer in the form abc with no spaces, in which the a, b, c refer to the exponents (powers) in $\mathrm{mol^a\,dm^b\,s^c}$.

Part B Complex general law

Another reaction has the rate law $r = \frac{k_1[A]^3[B]^2}{[C]}$. What are the units of k_1? Give your answer in the form abc with no spaces, in which the a, b, c refer to the exponents (powers) in $\mathrm{mol}^{\mathrm{a}}\ \mathrm{dm}^{\mathrm{b}}\ \mathrm{s}^{\mathrm{c}}$.

Part C Example reaction

$$\mathrm{CO} + \mathrm{Cl_2} \longrightarrow \mathrm{COCl_2}$$

This reaction has the rate law $r = k_2[\mathrm{CO}][\mathrm{Cl_2}]^{\frac{3}{2}}$.

What are the units of k_2? Give your answer in the form $2a\,2b\,2c$ with no spaces, in which the a, b, c refer to the exponents (powers) in $\mathrm{mol}^{\mathrm{a}}\,\mathrm{dm}^{\mathrm{b}}\,\mathrm{s}^{\mathrm{c}}$.

Part D Zeroth order

The reaction

$$2\,\mathrm{NH_3\,(g)} \xrightarrow{\mathrm{Pt}} \mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)}$$

follows zeroth order reaction kinetics. What are the units of the rate constant k_3?

- $\mathrm{mol\,s^{-1}}$
- $\mathrm{mol\,dm^{-3}\,s^{-1}}$
- $\mathrm{mol\,dm^{-3}}$
- $\mathrm{s^{-1}}$
- $\mathrm{mol\,dm^{-3}\,s^{-2}}$
- $\mathrm{mol^2\,dm^{-6}\,s^{-1}}$

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Temperature Variation

A Level

Two substances, X and Y, react in an inert solvent according to the following equation:

$\mathrm{X} + 2\,\mathrm{Y} \longrightarrow \mathrm{XY_2}$.

The following experiments were run to determine the order of the reaction between X and Y, at $20\,^\circ\mathrm{C}$.

Experiment number	Initial concentration of $\mathrm{X}/\mathrm{mol\,dm^{-3}}$	Initial concentration of $\mathrm{Y}/\mathrm{mol\,dm^{-3}}$	Initial rate of formation of $\mathrm{XY_2}/\mathrm{mol\,dm^{-3}\,min^{-1}}$
1	0.10	0.10	0.0010
2	0.10	0.20	0.0040
3	0.10	0.30	0.0090
4	0.15	0.10	0.0010
5	0.20	0.20	?

Part A Order of the reaction

What is the order of the reaction with respect to X and Y, respectively?

- 0; 2
- 0; 1
- -1; -1
- 2; 1
- 1; 0
- 1; 2

Part B Rate constant

Calculate the numerical value for the rate constant k.

Part C Initial rate of experiment 5

Predict the rate of formation of $\mathrm{XY_2}$ in experiment 5.

Part D Greatest reaction rate

The rate constant has an Arrhenius dependence on temperature. Knowing that the activation energy for the reaction is $53\,\mathrm{kJ\,mol^{-1}}$, which of the following sets of conditions will give the greatest rate of reaction?

- $[X] = 0.3\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.1\,\mathrm{mol\,dm^{-3}}$, $t = 30\,^\circ\mathrm{C}$.
- $[X] = 0.1\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.2\,\mathrm{mol\,dm^{-3}}$, $t = 40\,^\circ\mathrm{C}$.
- $[X] = 0.1\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.3\,\mathrm{mol\,dm^{-3}}$, $t = 30\,^\circ\mathrm{C}$.
- $[X] = 0.2\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.2\,\mathrm{mol\,dm^{-3}}$, $t = 30\,^\circ\mathrm{C}$.
- $[X] = 0.3\,\mathrm{mol\,dm^{-3}}$, $[Y] = 0.1\,\mathrm{mol\,dm^{-3}}$, $t = 20\,^\circ\mathrm{C}$.

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Thiosulfate Reactions

Sodium thiosulfate is an immensely useful chemical. It is on the World Health Organisation's List of Essential Medicines, a list of the most important medications needed in a basic health system.

It is also used in hand warmers and, usefully for this question, kinetics experiments.

Part A Reaction equation

When sodium thiosulfate solution reacts with dilute hydrochloric acid, the solution becomes cloudy. The equation for this reaction is given below.

$$\mathrm{Na_2S_2O_3\,(aq) + 2\,HCl\,(aq) \longrightarrow 2\,NaCl\,(aq) + H_2O\,(l) + SO_2\,(g) + S\,(s)}$$

Which species causes the solution to become cloudy?

- $\mathrm{H_2O\,(l)}$
- $\mathrm{NaCl\,(aq)}$
- $\mathrm{SO_2\,(g)}$
- $\mathrm{S\,(s)}$

Part B Rate estimate

A chemist conducted an experiment to investigate how the concentration of $S_2O_3^{2-}(aq)$ affects the time taken for the solution to become cloudy. Their results are as follows:

Concentration of sodium thiosulfate / $\mathrm{mol\,dm^{-3}}$	Time taken for the solution to become cloudy / seconds
0.040	69
0.060	44
0.080	35

Given that a good estimate of the rate of the reaction is given by:

$$\frac{1}{\text{time taken for solution to become cloudy}}$$

Calculate the rate when the concentration of sodium thiosulfate is $0.040\,\mathrm{mol\,dm^{-3}}$.

Part C Introduction to orders

The order of reaction with respect to a reactant indicates how much the rate changes with a change in the concentration of a reactant.

- In a zeroth order reaction, doubling the concentration of the reactant has no effect on the rate of the reaction.
- In a first order reaction, doubling the concentration of the reactant doubles the rate of reaction.
- In a second order reaction, doubling the concentration of the reactant quadruples the rate of reaction.
- And so on.

By calculating the rate of reaction when the concentration of $S_2O_3^{2-}$ is $0.080\,\mathrm{mol\,dm^{-3}}$, and comparing this with the value when the concentration is $0.040\,\mathrm{mol\,dm^{-3}}$, calculate the order of the reaction with respect to sodium thiosulfate.

Part D Variability

Other than mistakes in measurement, which of the following options may have caused the non-exactness of the order you found in the previous question?

- The sulfur formed can begin to react with the dilute hydrochloric acid.
- Sulfur can dissolve in the water.
- The SO_2 formed is denser than air, so will sit in the flask and make the solution look more cloudy.
- Temperature variation during the experiment.

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