SciFun

Chemical Kinetics – 2

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Recap

Chemical kinetics is the area of chemistry that deals reaction mechanisms and rates

You need to identify what changes in your sample as the chemical reaction proceeds in order to choose the most suitable method for measuring the reaction rate. One very common method is UV–visible spectroscopy.

Definition of reaction rate

⚠

$$r = \frac{1}{\xi_P}\frac{\Delta[\text{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\text{Reactant}]}{\Delta t}$$

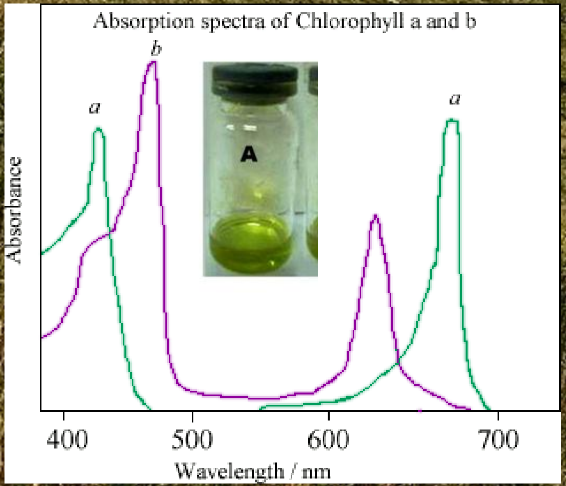
Beer law

⚠ $A = \varepsilon \cdot l \cdot [\text{Ch}]$

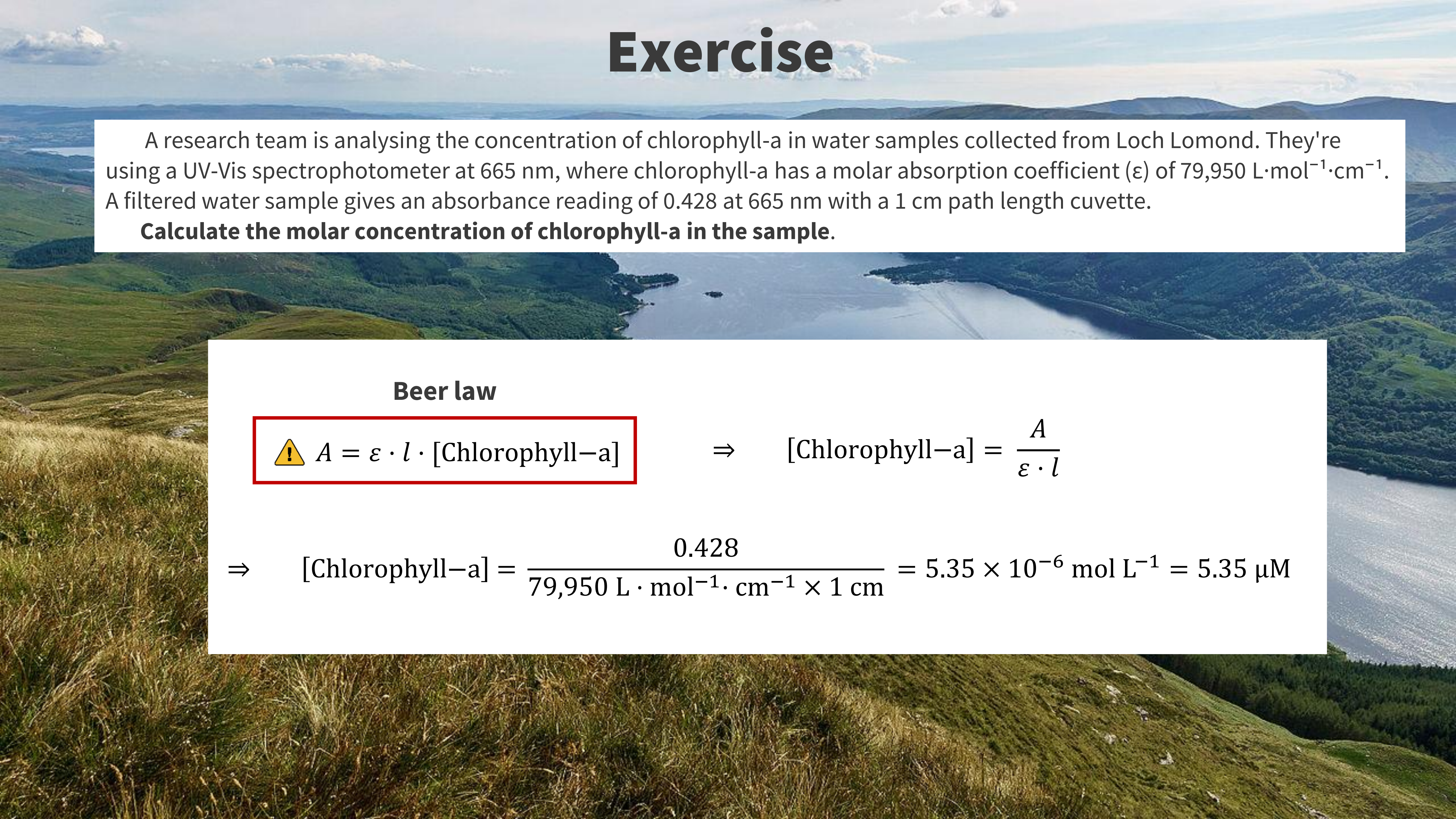
Exercise

A research team is analysing the concentration of chlorophyll-a in water samples collected from Loch Lomond. They're using a UV-Vis spectrophotometer at 665 nm, where chlorophyll-a has a molar absorption coefficient (ε) of 79,950 $L\cdot mol^{-1}\cdot cm^{-1}$. A filtered water sample gives an absorbance reading of 0.428 at 665 nm with a 1 cm path length cuvette.

Calculate the molar concentration of chlorophyll-a in the sample.



Exercise



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Calculate the molar concentration of chlorophyll-a in the sample.

Beer law

$$\boxed{⚠\ A = \varepsilon \cdot l \cdot [\mathrm{Chlorophyll{-}a}]} \quad \Rightarrow \quad [\mathrm{Chlorophyll{-}a}] = \frac{A}{\varepsilon \cdot l}$$

$$\Rightarrow \quad [\mathrm{Chlorophyll{-}a}] = \frac{0.428}{79{,}950\ \mathrm{L \cdot mol^{-1} \cdot cm^{-1}} \times 1\ \mathrm{cm}} = 5.35 \times 10^{-6}\ \mathrm{mol\ L^{-1}} = 5.35\ \mathrm{\mu M}$$

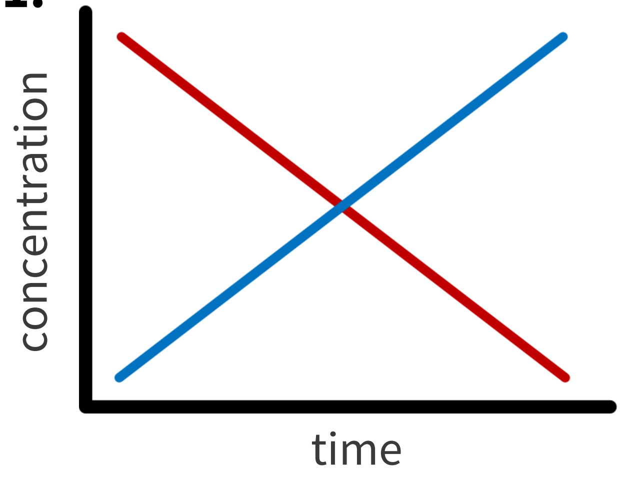
Challenge question

We have two reactants that undergo the following reaction to form a product.

$$A + B \longrightarrow C$$

Using one of the (somewhat imaginative) analytical techniques discussed earlier, we have been able to determine how the concentration of one reactant and the product evolve over time. If we plot these concentrations as a function of time, what would the graph look like?

1.



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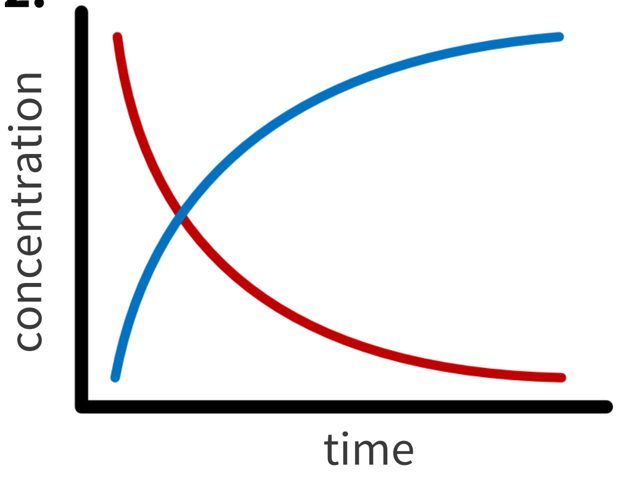
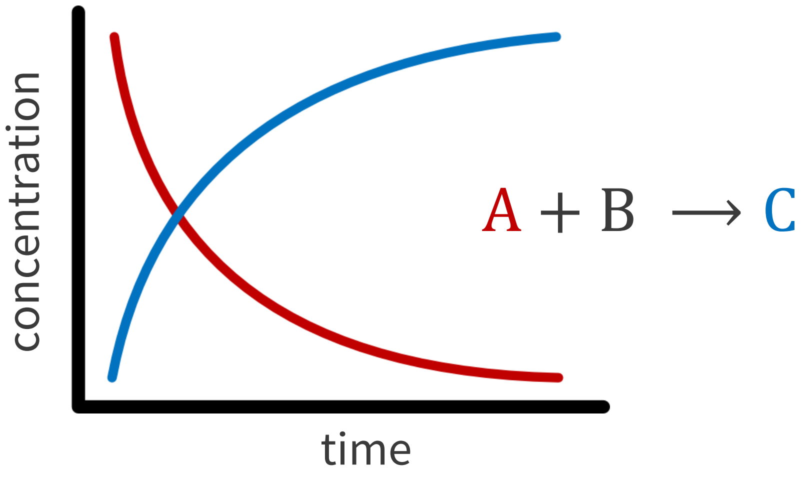
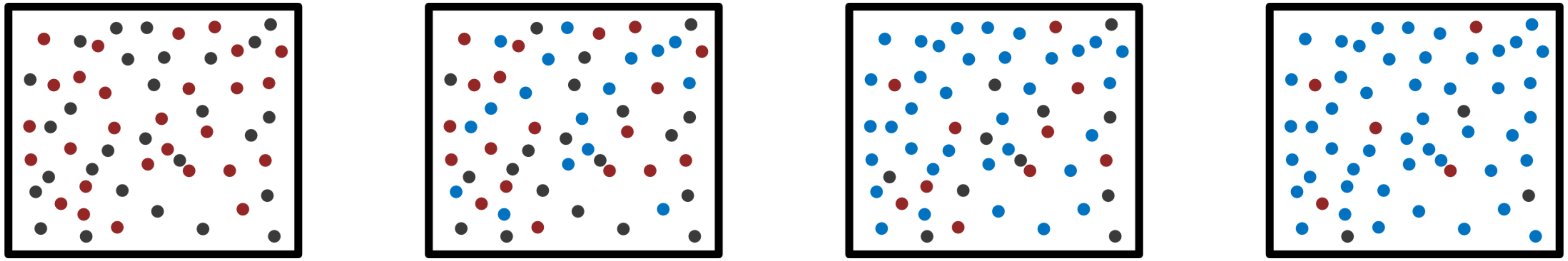


Challenge question: the answer

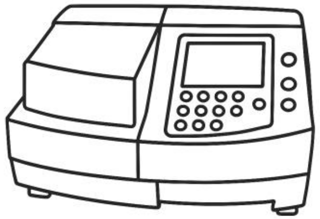
2.



As the reaction proceeds, the reactants are being consumed. Since the reaction rate depends on each reactant concentration, the rate is highest at the start (when the reactants concentrations are largest) and decreases over time. This leads to non-linear (curved) concentration–time profiles



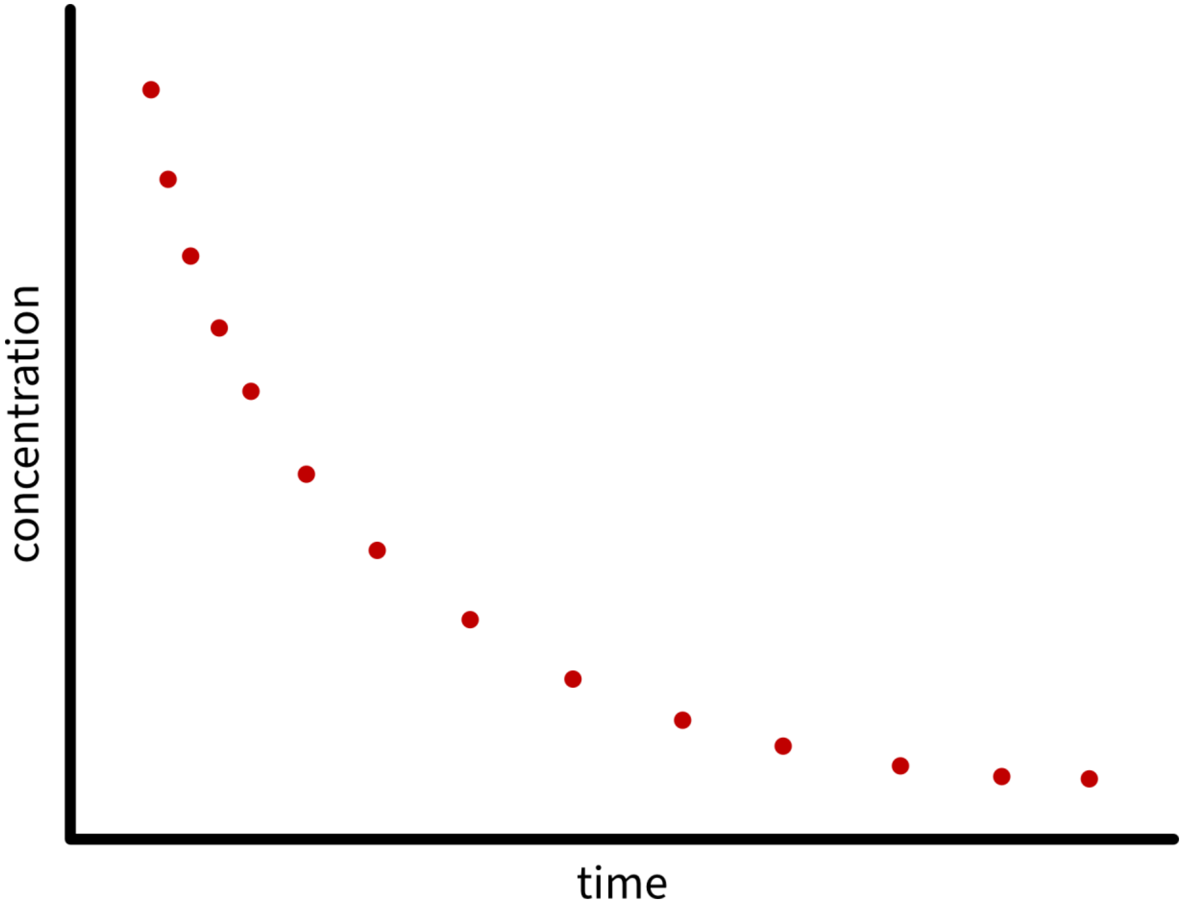
How to determine the reaction rate experimentally



spectrometer

$$A = \varepsilon \cdot l \cdot [\mathrm{Ch}]$$

$$r = \frac{1}{\xi_P}\frac{\Delta[\mathrm{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\mathrm{Reactant}]}{\Delta t}$$



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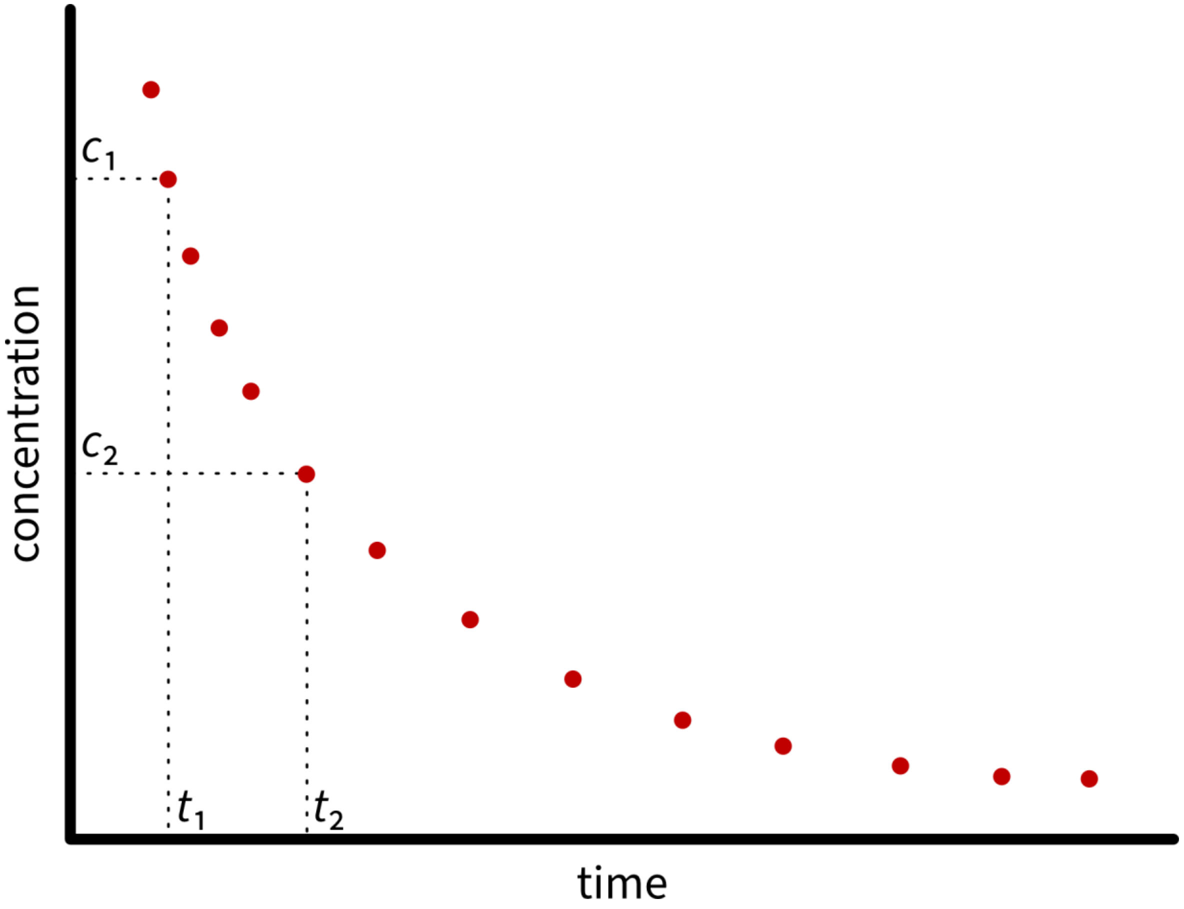

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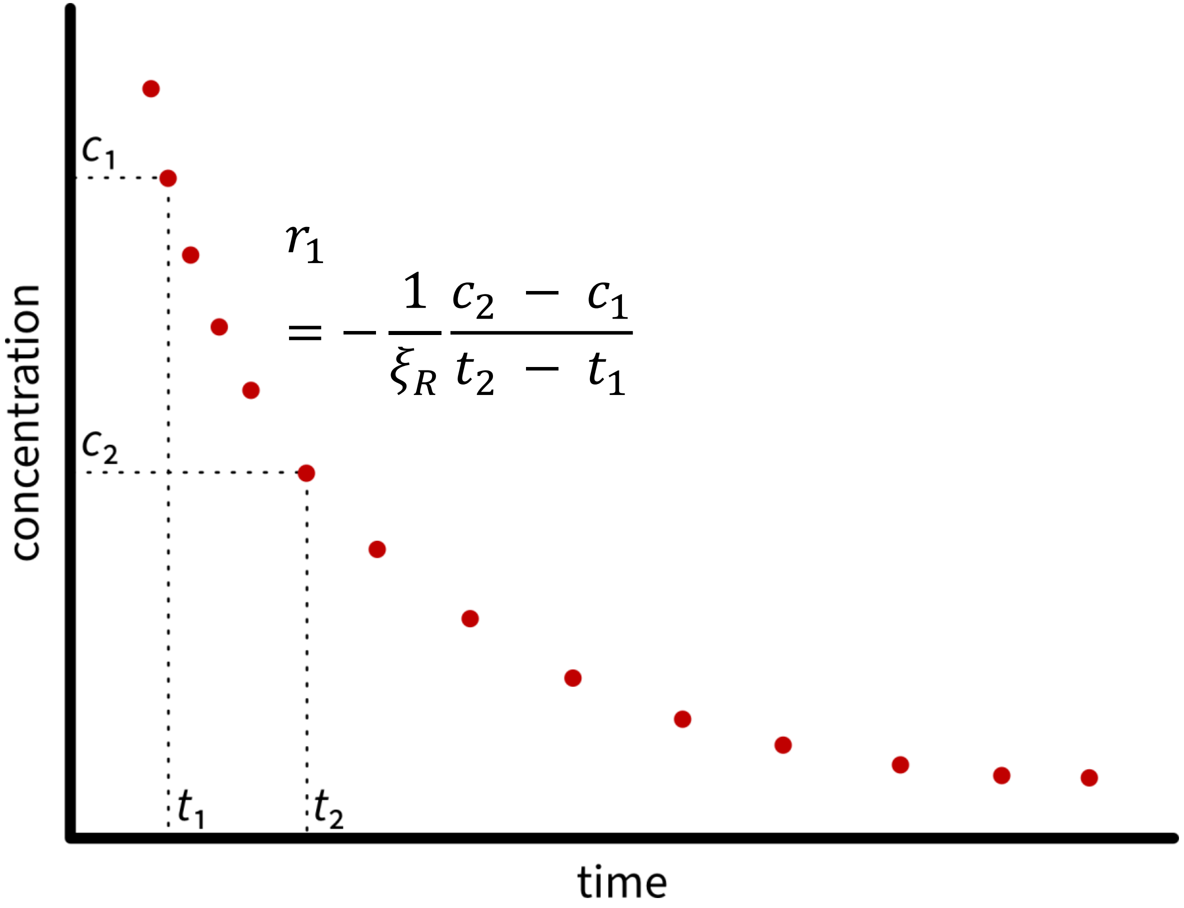

$$r_1 = -\frac{1}{\xi_R}\frac{c_2 - c_1}{t_2 - t_1}$$

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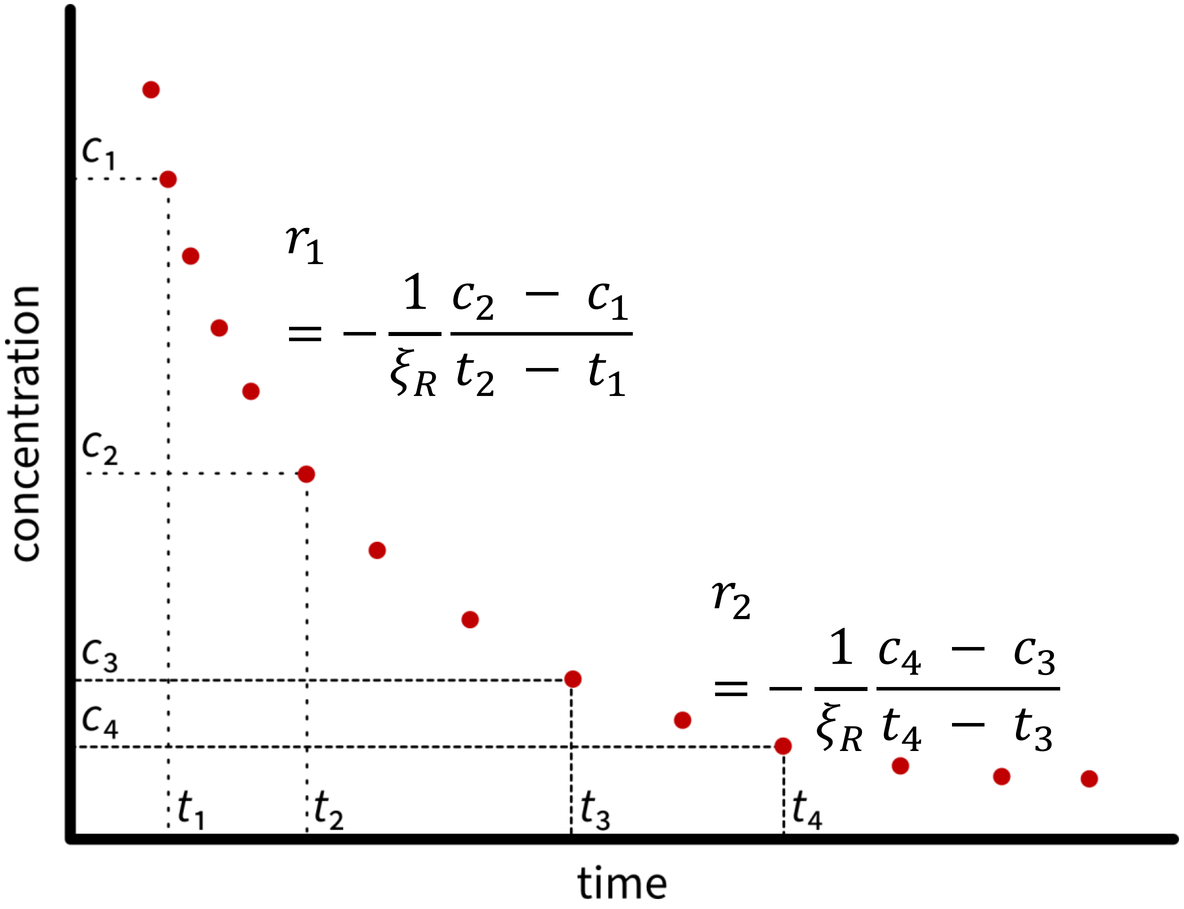
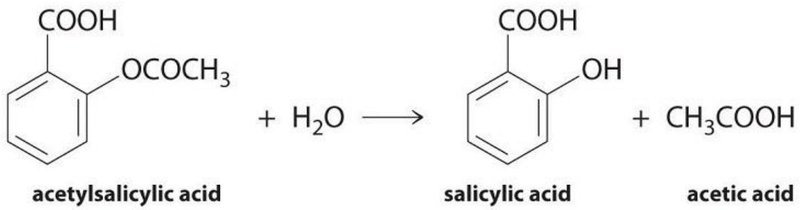


$$r_1 = -\frac{1}{\xi_R}\frac{c_2 - c_1}{t_2 - t_1}$$

$$r_2 = -\frac{1}{\xi_R}\frac{c_4 - c_3}{t_4 - t_3}$$

Exercise

A pharmaceutical company in Dundee is studying the hydrolysis of aspirin (acetylsalicylic acid) in aqueous solution at 37°C. This reaction is clinically relevant as it determines how quickly aspirin degrades in the body and in stored solutions. The hydrolysis reaction is:



A technician monitors the concentration of acetylsalicylic acid over time using HPLC. The results are:

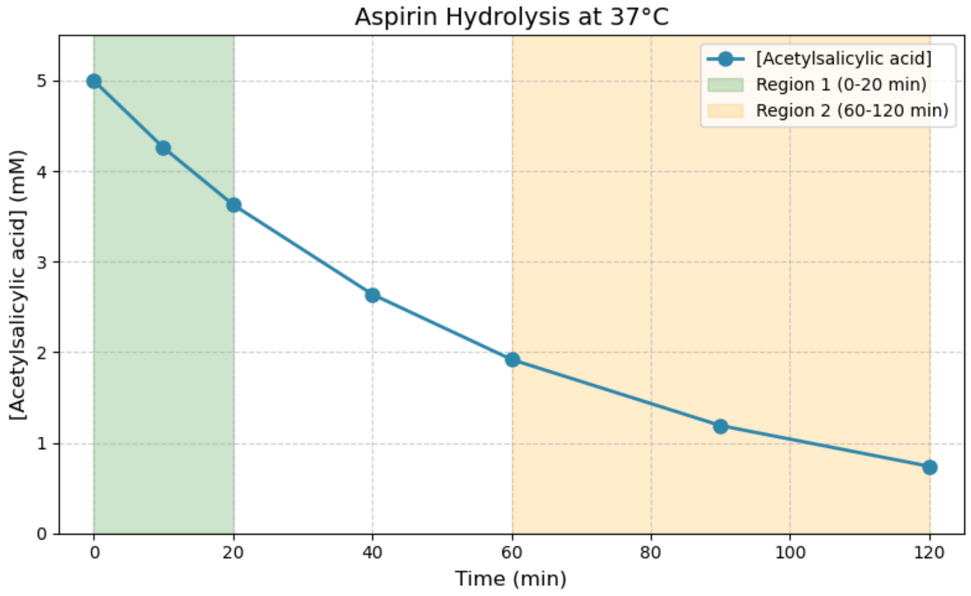
Time / min	[Acetilsalicilic acid] / mM
0	5.00
10	4.26
20	3.63
40	2.64
60	1.92
90	1.19
120	0.74

Calculate the average rate of disappearance of acetylsalicylic acid between:

$t = 0$ and $t = 20$ min
$t = 60$ and $t = 120$ min

Express your answers in $\text{mM}\cdot\text{min}^{-1}$ and comment on how the rate changes as the reaction progresses.

Exercise



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t = 60 and t = 120 min

$$r = \frac{1}{\xi_P}\frac{\Delta[\text{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\text{Reactant}]}{\Delta t}$$

First stage:

$$r_1 = -\frac{[\text{ASA}]_{20} - [\text{ASA}]_0}{20 - 0}$$

$$r_1 = -\frac{3.63\ \text{mM} - 5.00\ \text{mM}}{20\ \text{min}}$$

$$r_1 = -\frac{-1.37\ \text{mM}}{20\ \text{min}}$$

$$r_1 = 0.0685\ \text{mM}{\cdot}\text{min}^{-1}$$

Second stage:

$$r_2 = -\frac{0.74\ \text{mM} - 1.92\ \text{mM}}{60\ \text{min}}$$

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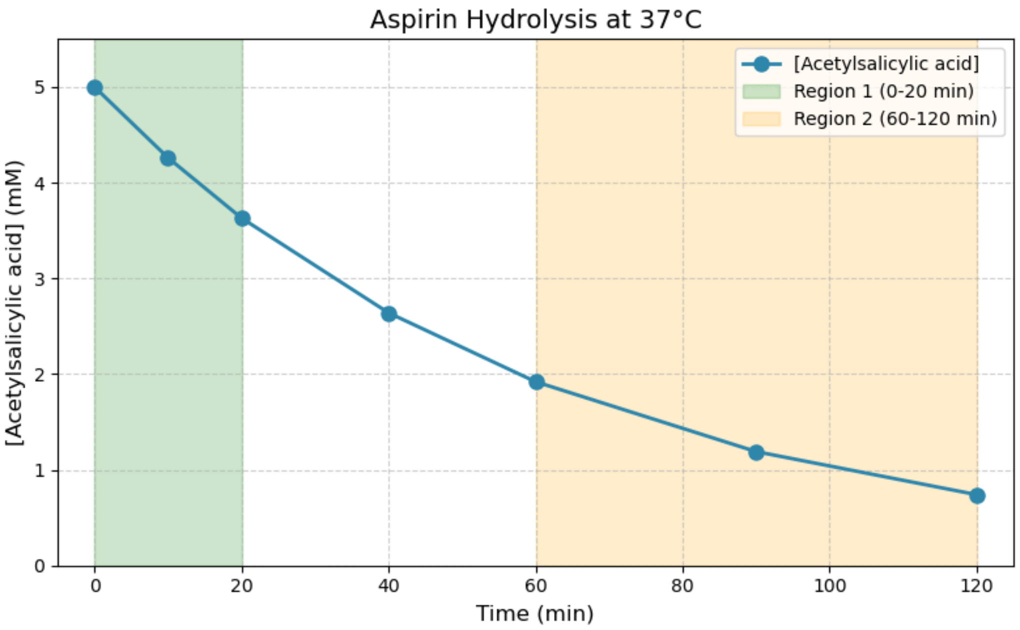
$$r_2 = 0.0197\ \text{mM}{\cdot}\text{min}^{-1}$$

Exercise



Comment on how the rate changes as the reaction progresses

$$r_1 = -\frac{[\mathrm{ASA}]_{20} - [\mathrm{ASA}]_0}{20 - 0}$$

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$$r_2 = -\frac{-1.18\ \mathrm{mM}}{60\ \mathrm{min}}$$

$$r_2 = 0.0197\ \mathrm{mM{\cdot}min}^{-1}$$

$$\frac{r_1}{r_2} = \frac{0.0685}{0.0197} \approx 3.5$$

The reaction is approximately 3.5 times faster at the beginning than in the final stage. As acetylsalicylic acid is consumed, fewer molecules remain available to react, which reduces the reaction rate.

I want my rate

NOW

Something that has kept many people awake at night

a.k.a. Philosophy

If any portion of time be conceived which cannot now be divided into even the minutest particles of moments, this only is that which may be called present; which, however, flies so rapidly from future to past, that it cannot be extended by any delay. For if it be extended, it is divided into the past and future; but the present hath no space.

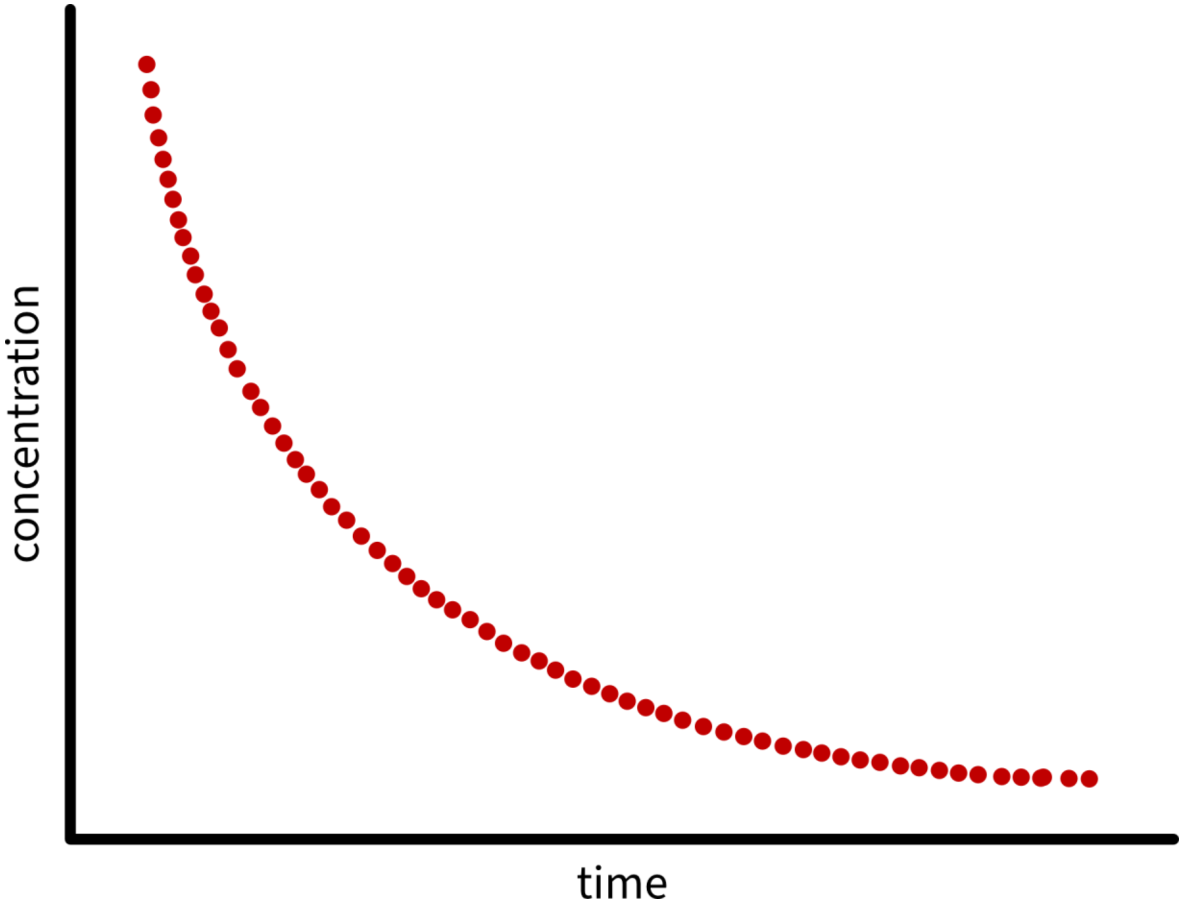
Where, therefore, is the time which we may call long? Is it nature? Indeed we do not say, "It is long," because it is not yet, so as to be long; but we say, "It will be long." When, then, will it be? For if even then, since as yet it is future, it will not be long, because what may be long is not as yet; but it shall be long, when from the future, which as yet is not, it shall already have begun to be, and will have become present, so that there could be that which may be long; then doth the present time cry out in the words above that it cannot be long. […]

But how do we measure present time, since it hath not space? It is measured while it passeth; but when it shall have passed, it is not measured; for there will not be aught that can be measured. But whence, in what way, and whither doth it pass while it is being measured? Whence, but from the future? Which way, save through the present? Whither, but into the past? From that, therefore, which as yet is not, through that which hath no space, into that which now is not.

Augustine of Hippo, The Confessions
(chapters XVII and XXI)

How to determine the instantaneous reaction rate experimentally

$$r = \frac{1}{\xi_P}\frac{\Delta[\mathrm{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\mathrm{Reactant}]}{\Delta t}$$



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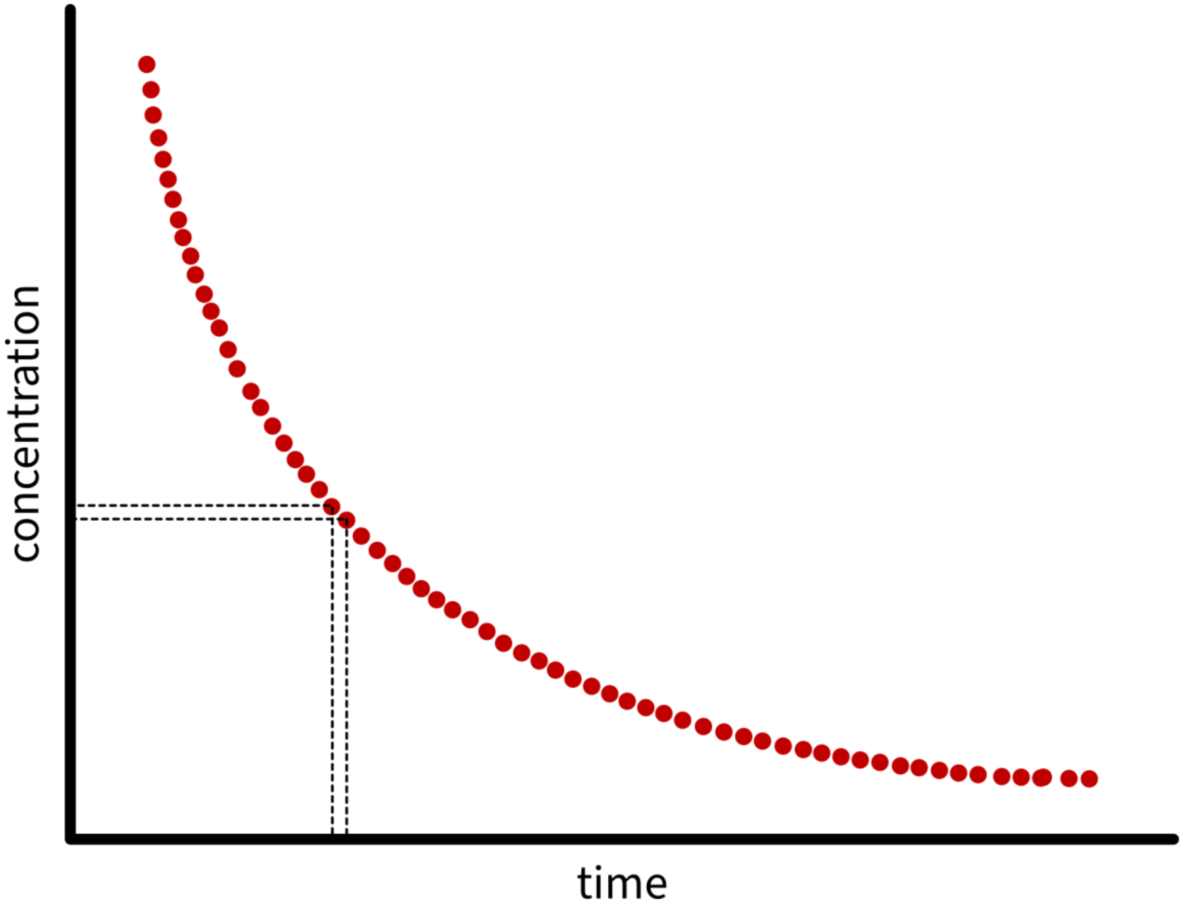
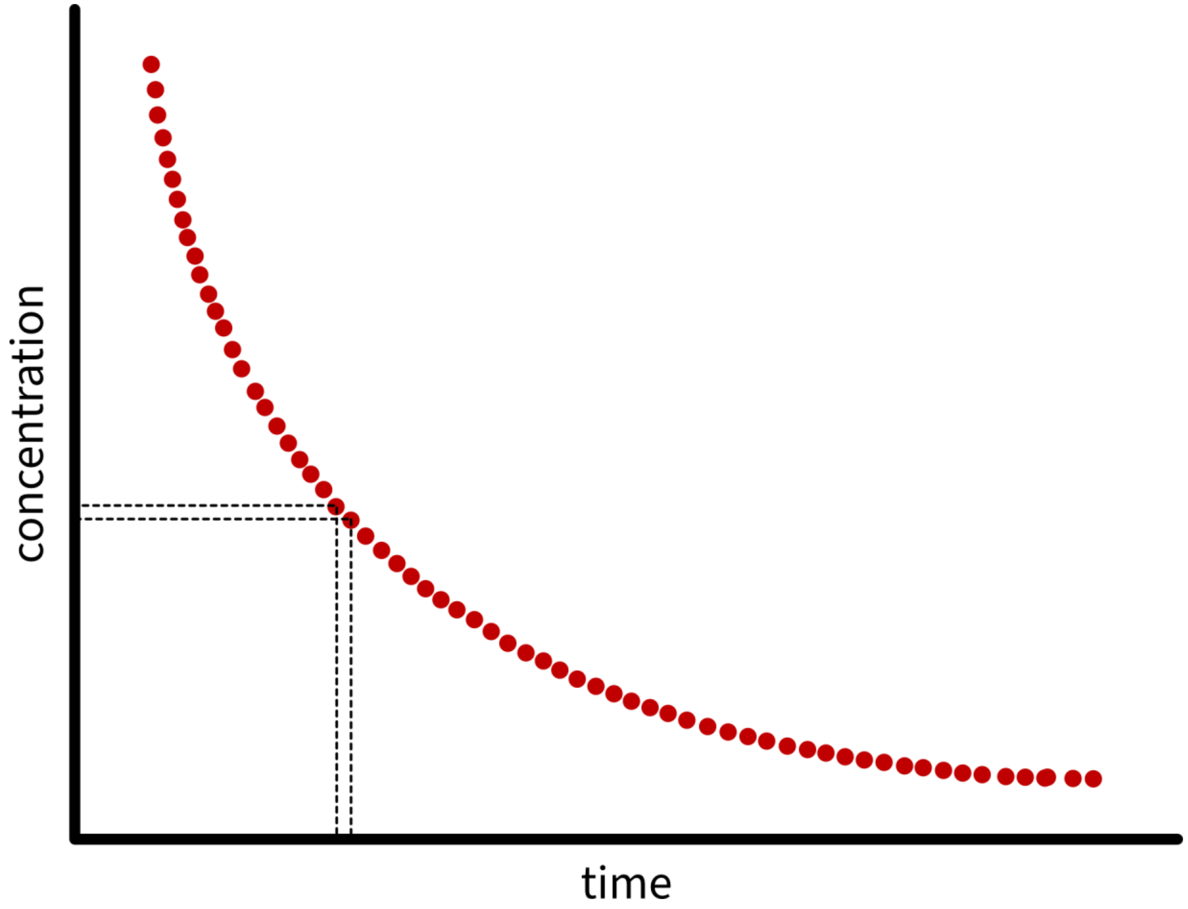


How to determine the instantaneous reaction rate experimentally

$$r_{\text{inst}} = \lim_{\Delta t \to 0} -\frac{1}{\xi_r} \frac{\Delta[\text{Reactive}]}{\Delta t}$$



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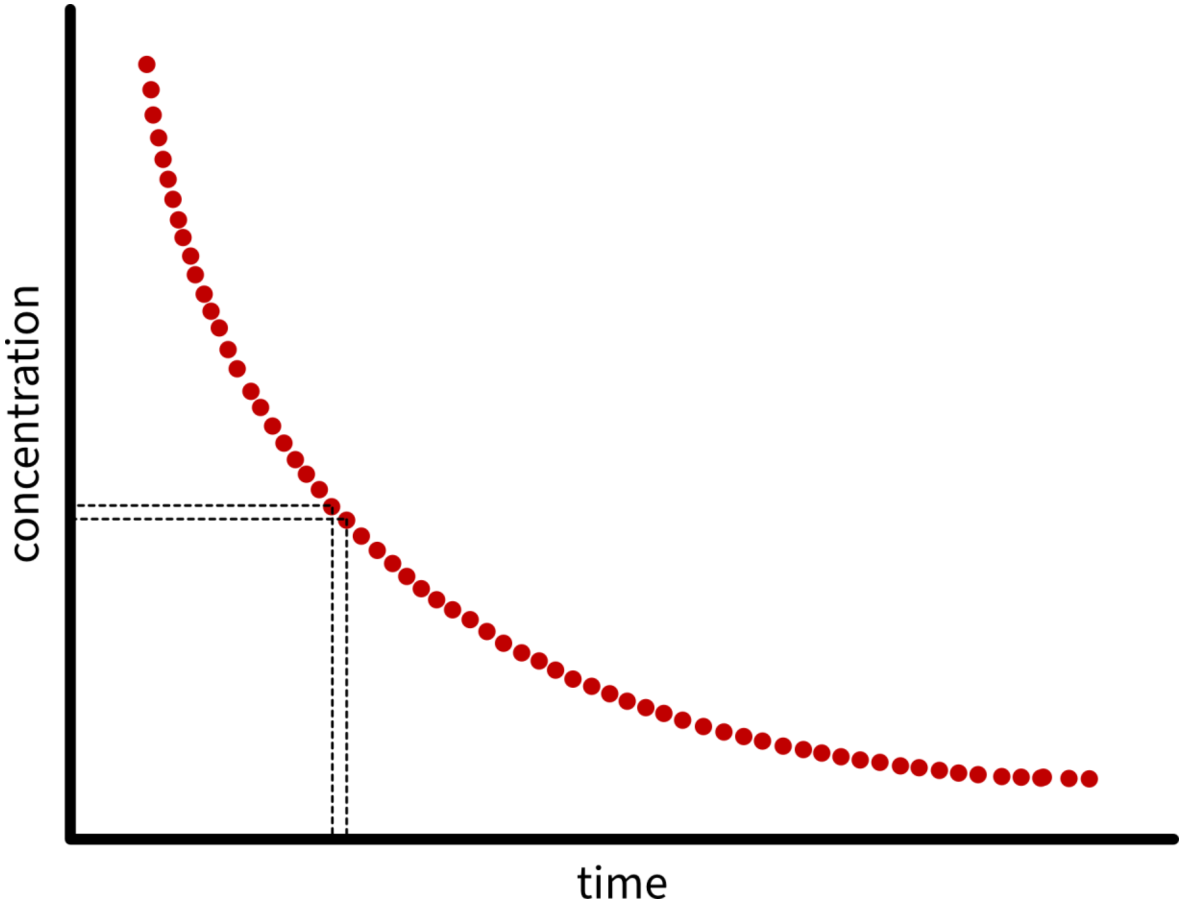
$$r_{\text{inst}} = \lim_{\Delta t \to 0} -\frac{1}{\xi_r}\frac{\Delta[\text{Reactive}]}{\Delta t} = -\frac{1}{\xi_r}\frac{d[\text{Reactive}]}{dt}$$



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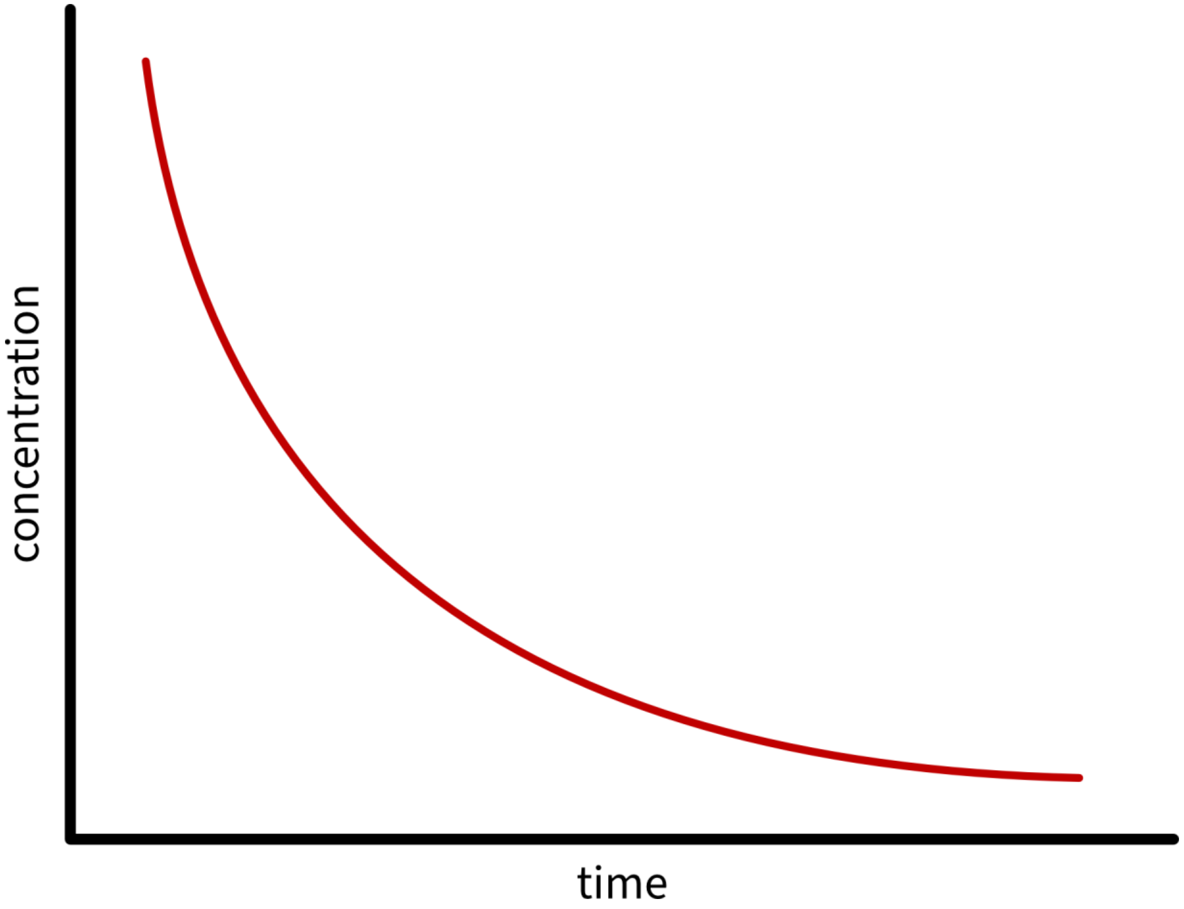

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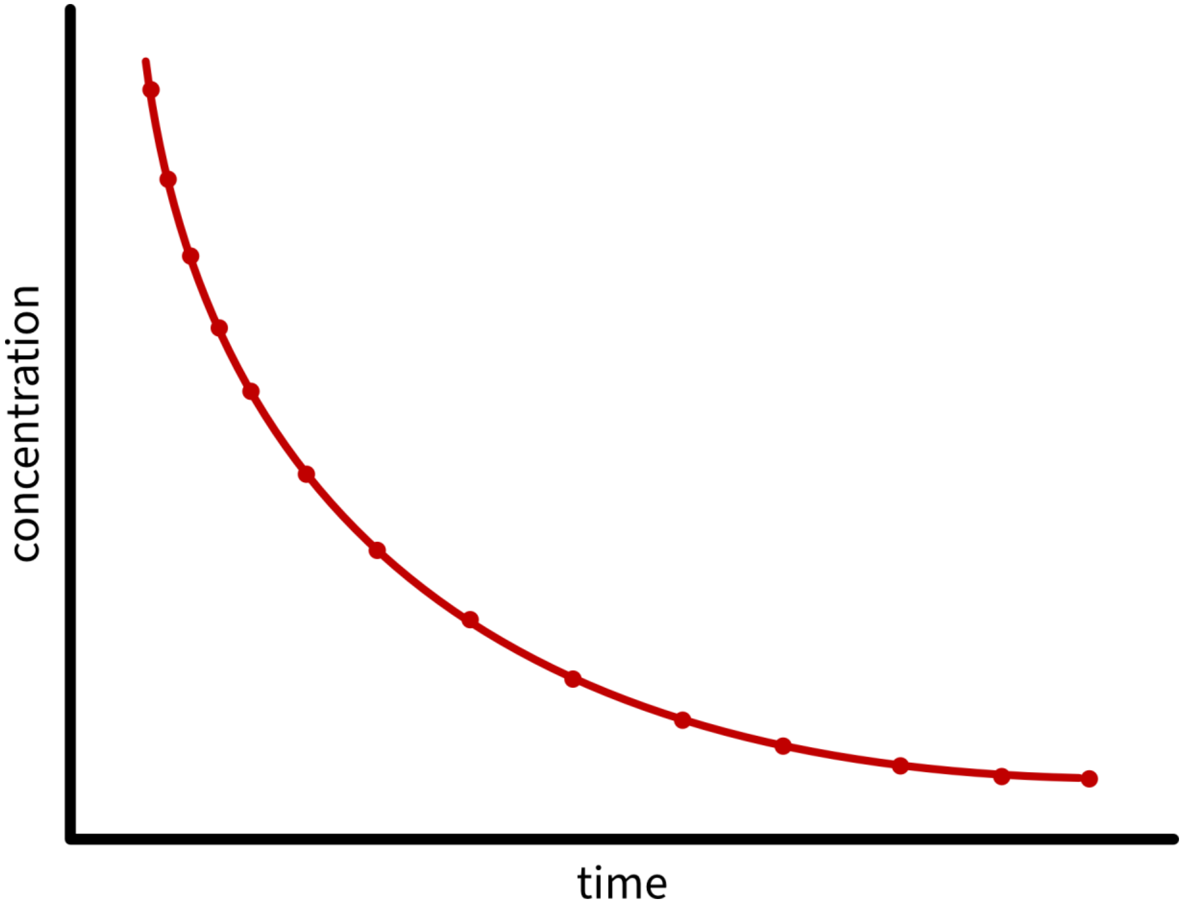


Rate law

To describe the curve we need a function that depends only on the concentration of the reactants

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \qquad\qquad r = -\frac{1}{\xi_R}\frac{d[\mathrm{Reactant}]}{dt} = f([\mathrm{A}],[\mathrm{B}])$$

There is a large class of chemical reactions in which the forward reaction rate is proportional to the concentration of each reactant raised to some power.

⚠

$$\boxed{r = -\frac{1}{\xi_R}\frac{d[\mathrm{Reactant}]}{dt} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}}$$

where:

α is the order with respect to substance A

β is the order with respect to substance B.

The sum of the orders with respect to the different substances is called the **overall order**.

📖 Reaction order: Reaction order is the power to which a reactant concentration is raised in the rate law, indicating how the reaction rate depends on that concentration. It is not necessarily equal to the stoichiometric coefficient of the reactant. The orders are usually small positive integers, but other cases do occur

Exercises

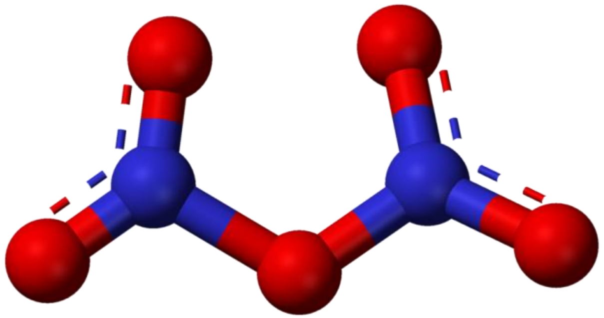
The thermal decomposition of dinitrogen pentoxide in the gas phase:

$$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

Experimentally, the following rate law is found:

$$r = k[N_2O_5]$$

a) What is the partial order with respect to N_2O_5?
b) What is the overall order of the reaction?



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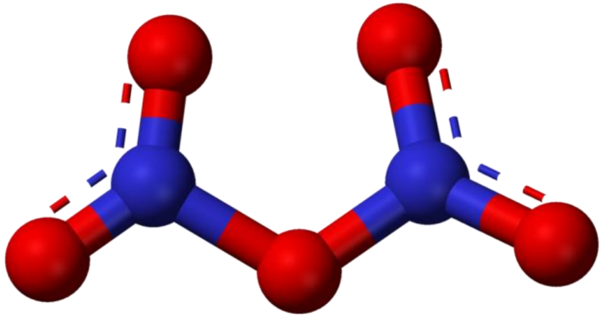

Experimentally, the following rate law is found:

$$r = k[N_2O_5]$$

a) What is the partial order with respect to N_2O_5?

The reaction is first order with respect to N_2O_5

b) What is the overall order of the reaction?

The reaction is first order overall

Exercises

The gas-phase reaction between nitric oxide and oxygen:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The experimentally determined rate law is:

$$r = k[NO]^2[O_2]$$

a) What is the partial order with respect to NO?
b) What is the partial order with respect to O_2?
c) What is the overall order of the reaction?

Nitrogen dioxide: 2020 Beirut explosion

Exercises

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$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The experimentally determined rate law is:

$$r = k[NO]^2[O_2]$$

a) What is the partial order with respect to NO?

The reaction is second order with respect to NO

b) What is the partial order with respect to O_2?

The reaction is first order with respect to oxygen

c) What is the overall order of the reaction?

The reaction is third order overall

Nitrogen dioxide: 2020 Beirut explosion

Exercises

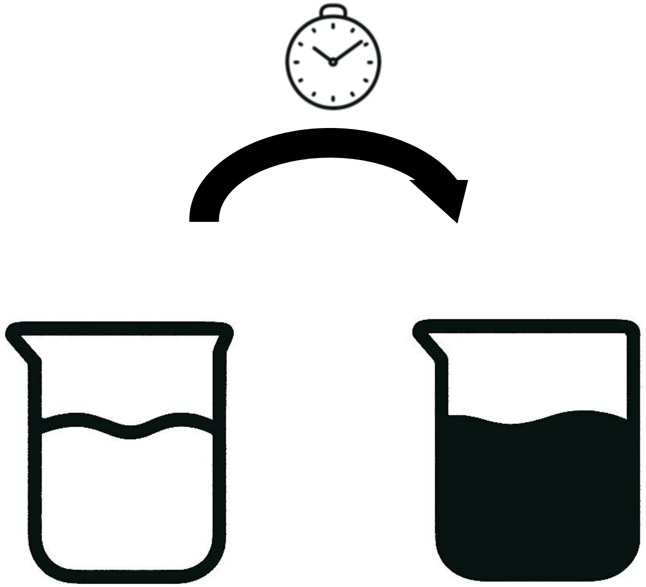
The reaction between persulfate and iodide ions in aqueous solution:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The experimentally determined rate law is:

$$r = k[S_2O_8^{2-}][I^-]$$

a) What is the partial order with respect to $S_2O_8^{2-}$?
b) What is the partial order with respect to I^-?
c) What is the overall order of the reaction?



Clock reaction

🍎 Resource in moodle: Video of a clock reaction

Exercises

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The experimentally determined rate law is:

$$r = k[S_2O_8^{2-}][I^-]$$

a) What is the partial order with respect to $S_2O_8^{2-}$?

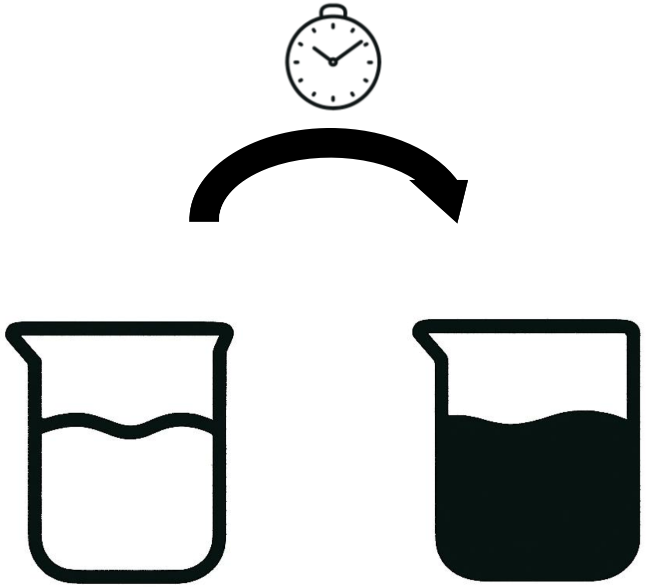
The reaction is first order with respect to $S_2O_8^{2-}$

b) What is the partial order with respect to I^-?

The reaction is first order with respect to I^-

c) What is the overall order of the reaction?

The reaction is second order overall



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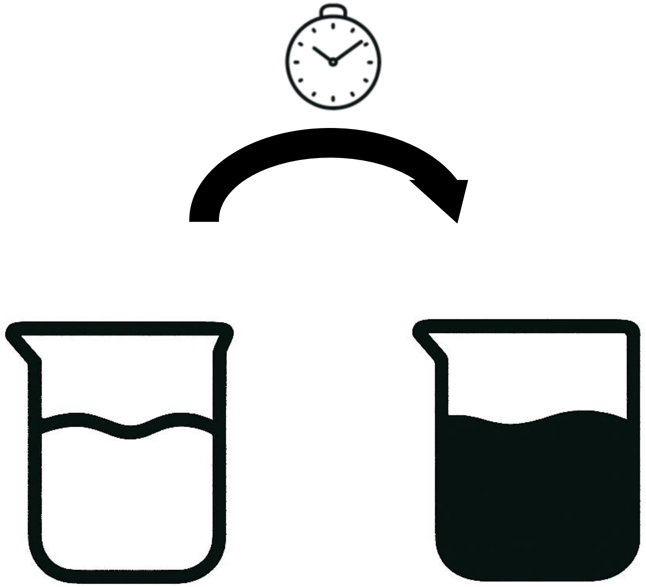
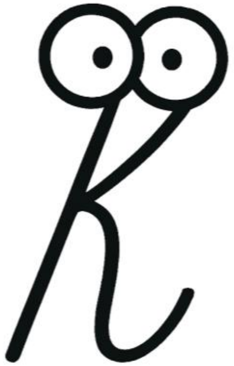
   The reaction is first order with respect to $S_2O_8^{2-}$
b) What is the partial order with respect to I^-?
   The reaction is first order with respect to I^-
c) What is the overall order of the reaction?
   The reaction is second order overall



Clock reaction

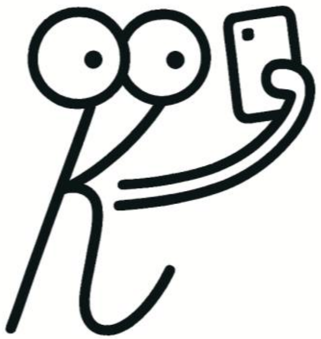
⚠ Remember! Reaction orders are determined experimentally and do not necessarily correspond to stoichiometric coefficients

Introducing k: Chemistry’s Biggest Influencer!



☑ Its name is **rate constant**, although its’s also known as specific rate because it’s the rate the reaction would have if all reactant concentrations were equal to one.

Introducing k: Chemistry's Biggest Influencer!



☑ Its name is **rate constant**, although its's also known as specific rate because it's the rate the reaction would have if all reactant concentrations were equal to one.

☑ It's completely independent of concentration, but very sensitive to temperature, pH or anything else that might change its mood.

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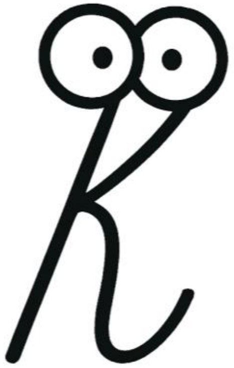


☑ Its name is **rate constant**, although its's also known as specific rate because it's the rate the reaction would have if all reactant concentrations were equal to one.

☑ It's completely independent of concentration, but very sensitive to temperature, pH or anything else that might change its mood.

☑ It's a rebel. As the reaction rate always has units of M s^{-1}, *k* refuses to stick to one set of units: they change with the overall reaction order.

Order 0

$$\frac{r}{[\mathrm{A}]^0} = k \quad (\mathrm{M\,s^{-1}})$$

Order 1

$$\frac{r}{[\mathrm{A}]} = k \quad (\mathrm{s^{-1}})$$

Order 2

$$\frac{r}{[\mathrm{A}][\mathrm{B}]} = k \quad (\mathrm{M^{-1}\,s^{-1}})$$

Order 3

$$\frac{r}{[\mathrm{A}][\mathrm{B}]^2} = k\,(\mathrm{M^{-2}\,s^{-1}})$$

How to experimentally measure *r*, α and *k*: The method of initial rates*

$$r = k[\mathrm{A}]^{\alpha}$$

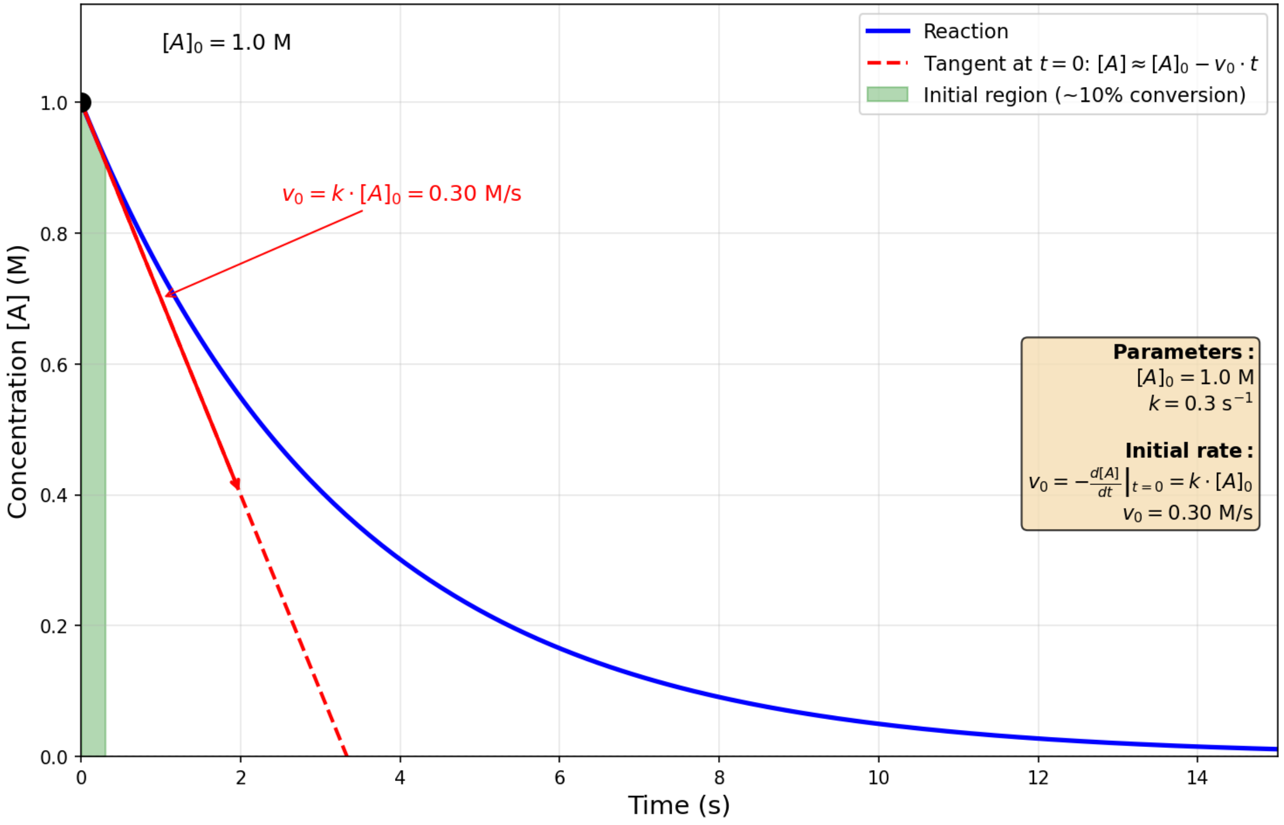
This method is based on an undeniable fact: the only time we know the exact concentration of A is at the very beginning, because we prepared the solution ourselves.

If, at the start of the reaction, we measure the reaction rate over a very short time such that $\Delta[\mathrm{A}] \lll [\mathrm{A}]_0$, that rate is very close to the instantaneous rate at time 0:

$$r_{t=0} = -\frac{1}{a}\left.\frac{d[\mathrm{A}]}{dt}\right|_{t=0} \approx -\frac{1}{a}\left.\frac{\Delta[\mathrm{A}]}{\Delta t}\right|_{t\to 0} = k[\mathrm{A}]_0^{\alpha}$$

* It is not limited to single-reactant systems.

Method of initial rates: the proof



$$r_{t=0} = -\frac{1}{a}\,\frac{d[\mathrm{A}]}{dt}\bigg|_{t=0} \approx -\frac{1}{a}\,\frac{\Delta[\mathrm{A}]}{\Delta t}\bigg|_{t\to 0} = k[\mathrm{A}]_0^{\alpha}$$

Method of initial rates: the use

$$r_{t=0} = k[\mathrm{A}]_0^{\alpha}$$

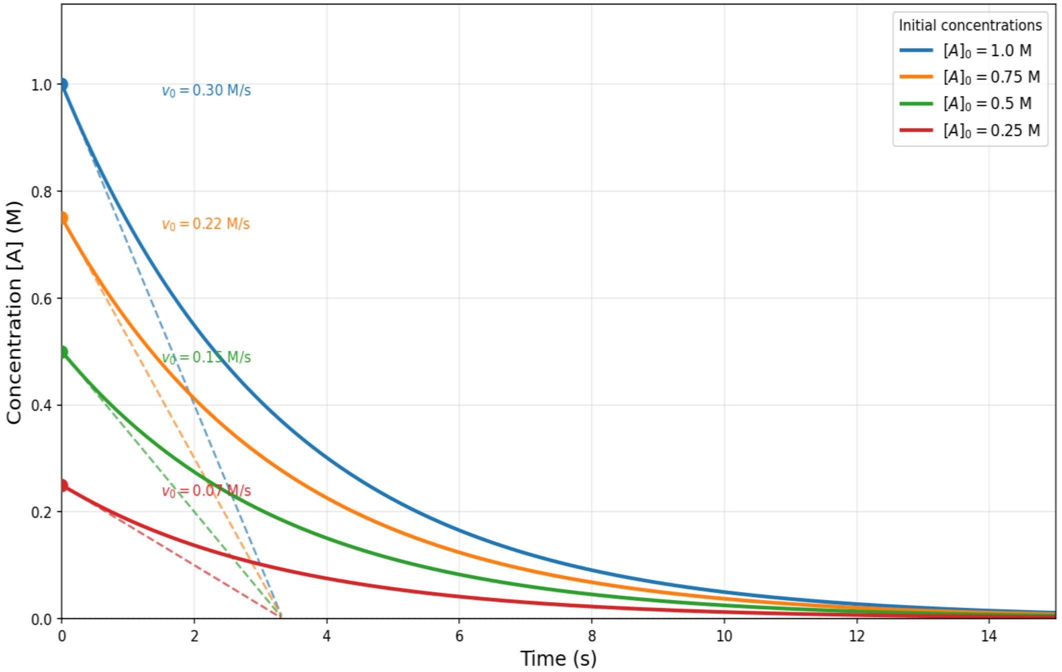
Method of initial rates: the use

$$r_{t=0} = k[\mathrm{A}]_0^{\alpha} \quad \Rightarrow \quad \ln(r_{t=0}) = \ln(k) + \alpha \ln([A]_0)$$

Method of initial rates: the use

$$r_{t=0} = k[\mathrm{A}]_0^{\alpha} \quad \Rightarrow \quad \ln(r_{t=0}) = \ln(k) + \alpha\ln([A]_0)$$

To minimize measurement errors, the initial rates are usually measured for several solutions with varying reactant concentrations:

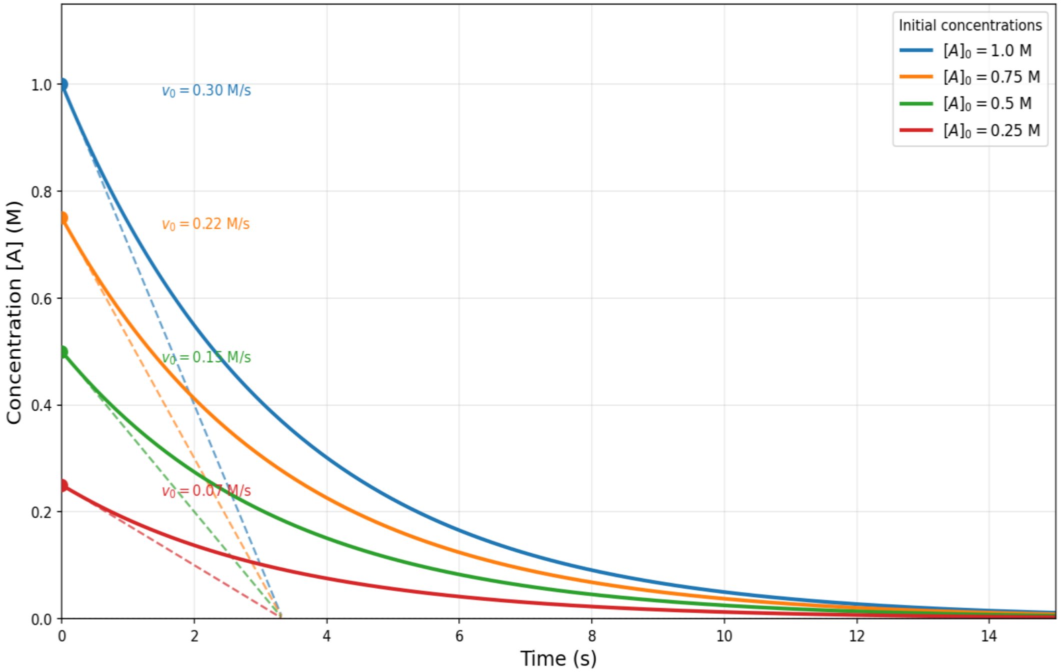


Concentration-time profiles

Method of initial rates: the use

$$r_{t=0} = k[\mathrm{A}]_0^{\alpha} \quad \Rightarrow \quad \ln(r_{t=0}) = \ln(k) + \alpha \ln([A]_0)$$

To minimize measurement errors, the initial rates are usually measured for several solutions with varying reactant concentrations:



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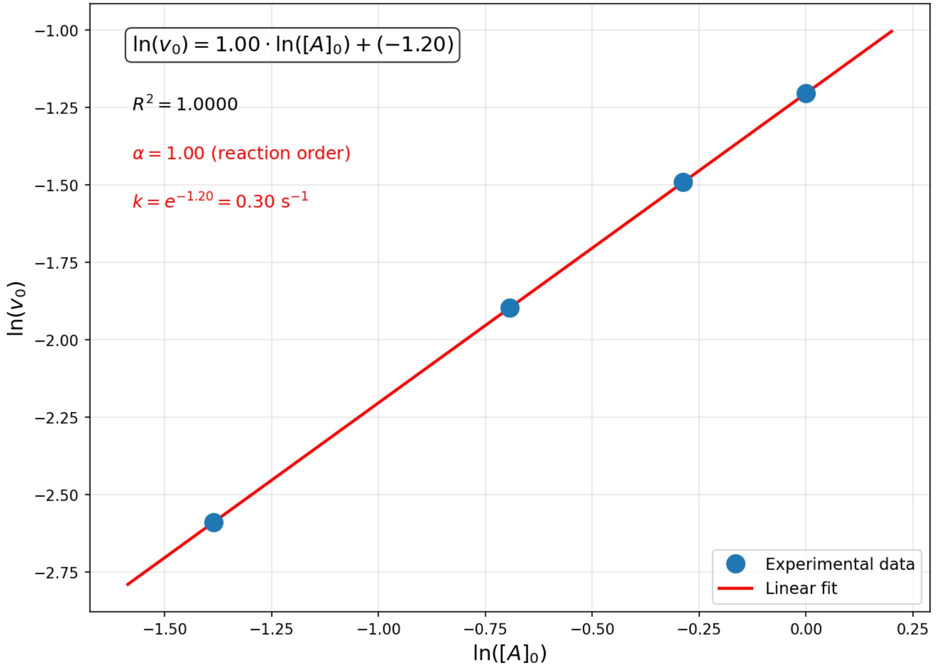

Linear regression

Challenge question(s)

The oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) is a key reaction in the formation of photochemical smog in urban areas. Vehicle exhaust releases NO into the atmosphere, where it reacts with oxygen:

$$2\mathrm{NO(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{NO_2(g)}$$

A series of experiments were performed in the laboratory, measuring the initial rate of NO_2 formation for different initial concentrations of NO and O_2:

Exp.	**$[NO]_0$ (mol·L^{-1})**	**$[O_2]_0$ (mol·L^{-1})**	**r_0 (mol·L^{-1}·s^{-1})**
1	2.0×10^{-4}	1.0×10^{-3}	2.8×10^{-9}
2	4.0×10^{-4}	1.0×10^{-3}	1.12×10^{-8}
3	2.0×10^{-4}	2.0×10^{-3}	5.6×10^{-9}
4	6.0×10^{-4}	3.0×10^{-3}	7.56×10^{-8}

a) Using experiments 1 and 2, determine the order of the reaction with respect to NO.
b) Using experiments 1 and 3, determine the order of the reaction with respect to O_2.
c) Write the complete rate law for this reaction.
d) Calculate the rate constant k and express it with the correct units.
e) Verify your rate law using the data from experiment 4
f) Explain why the reaction rate is particularly sensitive to the NO concentration (and therefore to the use of vehicles).