SCIFUN

CHEMICAL KINETICS 3 - MMXXVI

Mario González-Jiménez

Previously on Chemical Kinetics...

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

Definition of reaction rate

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

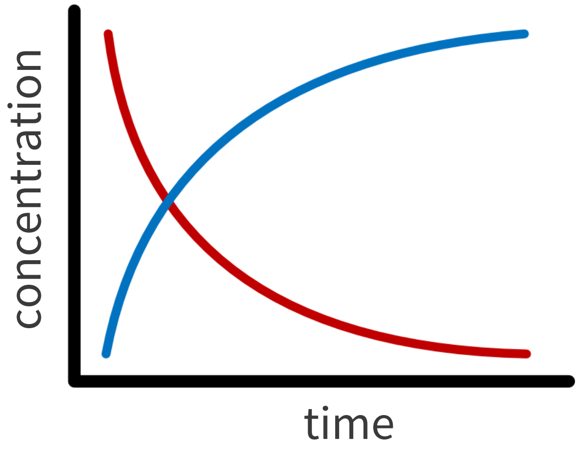
You need to identify what changes in your sample as the chemical reaction proceeds in order to choose the most suitable method for measuring the reaction rate. One very common method is UV–visible spectroscopy.

Beer law

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

Previously on Chemical Kinetics...

We need a function that depends only on the concentration of the reactants to describe how the rate changes with time



Rate law

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

Where:

$$k(T, pH, I, etc...)$$

α, β ≡ orders with respect to substances A and B
α + β ≡ overall order

Order 0

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

Order 1

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

Order 2

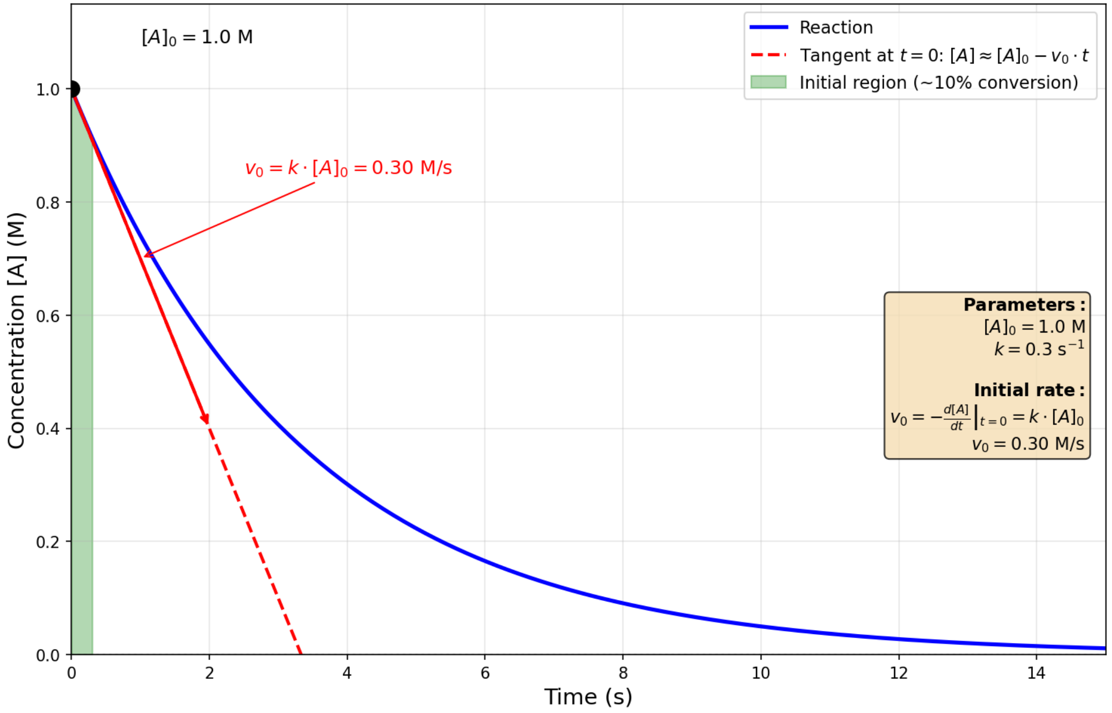
$$\frac{r}{[\text{A}][\text{B}]} = k \quad (\text{M}^{-1}\,\text{s}^{-1})$$

Order 3

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

Previously on Chemical Kinetics...

The method of initial rates determines the reaction order and rate constant by assuming that, at very short times, the measured average initial rate is equal to the instantaneous rate at time zero.



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

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:

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

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).

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

Oxidation of nitric oxide

a) Determine the order of the reaction with respect to O_2.

First, we prepare the rate law with the concentration of the reactants:

$$r = k[\mathrm{NO}]^{\alpha}[\mathrm{O_2}]^{\beta}$$

To find each partial order, we compare pairs of experiments where only one concentration changes:

NO: experiments 1 & 2

$$r_1 = k[\mathrm{NO}]_1^{\alpha}[\mathrm{O_2}]_1^{\beta}$$
$$r_2 = k[\mathrm{NO}]_2^{\alpha}[\mathrm{O_2}]_2^{\beta}$$

Since $[O_2]_1 = [O_2]_2$

$$\frac{r_2}{r_1} = \left(\frac{[\mathrm{NO}]_2}{[\mathrm{NO}]_1}\right)^{\alpha}$$

Solving for α:

$$\frac{1.12 \times 10^{-8}\ \mathrm{M \cdot s^{-1}}}{2.8 \times 10^{-9}\ \mathrm{M \cdot s^{-1}}} = \left(\frac{4.0 \times 10^{-4}\ \mathrm{M}}{2.0 \times 10^{-4}\ \mathrm{M}}\right)^{\alpha} \quad \Rightarrow \quad 4 = 2^{\alpha} \quad \Rightarrow \quad \alpha = 2$$

The reaction is second order with respect to NO

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

Oxidation of nitric oxide

b) Determine the order of the reaction with respect to NO.

I'm putting α in since we've already found it, though you don't actually need its value to solve this problem

$$r = k[\mathrm{NO}]^2[\mathrm{O_2}]^\beta$$

To find the partial order with respect to oxygen, we compare the experiments 1 and 3 where only the concentration of NO changes:

$$r_1 = k[\mathrm{NO}]_1^2[\mathrm{O_2}]_1^\beta$$
$$r_3 = k[\mathrm{NO}]_3^2[\mathrm{O_2}]_3^\beta$$

We divide:

$$\frac{r_3}{r_1} = \left(\frac{[\mathrm{O_2}]_3}{[\mathrm{O_2}]_1}\right)^\beta$$

Solving for β:

$$\frac{5.6 \times 10^{-9}\ \mathrm{M \cdot s^{-1}}}{2.8 \times 10^{-9}\ \mathrm{M \cdot s^{-1}}} = \left(\frac{2.0 \times 10^{-3}\ \mathrm{M}}{1.0 \times 10^{-3}\ \mathrm{M}}\right)^\beta \quad \Rightarrow \quad 2 = 2^\beta \quad \Rightarrow \quad \beta = 1$$

The reaction is first order with respect to O_2

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

Oxidation of nitric oxide

c) Write the complete rate law for this reaction

$$r = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

The overall order is α + β = 2 + 1 = 3 (third-order reaction)

d) Calculate the rate constant k and express it with the correct units.

First, we rearrange the rate law to isolate *k*:

$$k = \frac{r_0}{[\mathrm{NO}]^2[\mathrm{O_2}]}$$

Then, we substitute using, for example, experiment 1:

$$k = \frac{2.8 \times 10^{-9}\ \mathrm{M \cdot s^{-1}}}{(2.0 \times 10^{-4}\ \mathrm{M})^2 \times (1.0 \times 10^{-3}\ \mathrm{M})} = \frac{2.8 \times 10^{-9}\ \mathrm{M \cdot s^{-1}}}{4.0 \times 10^{-11}\ \mathrm{M^3}} = 70\ \mathrm{M^{-2} \cdot s^{-1}}$$

e) Verify your rate law using the data from experiment 4

$$r_{\mathrm{calc}} = 70\ \mathrm{M^{-2} \cdot\ s^{-1}} \times (6.0 \times 10^{-4}\ \mathrm{M})^2 \times (3.0 \times 10^{-3}\ \mathrm{M}) = 7.56 \times 10^{-8}\ \mathrm{M \cdot s^{-1}}$$

The rate law is confirmed!

Second order: so what

Explain why the reaction rate is particularly sensitive to the NO concentration (and therefore to the use of vehicles).

$$r = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

The reaction is second order with respect to NO, meaning that the rate does not scale linearly with [NO], but **quadratically**!!!

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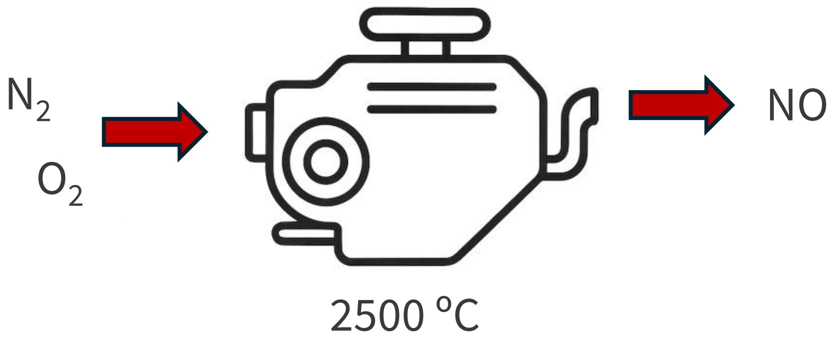

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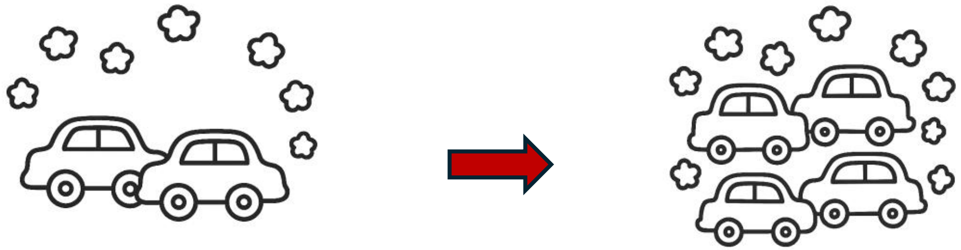

If [NO] doubles (×2) :
r increases by 2^2 = ×4

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If [NO] triples (×3) :
r increases by 3^2 = ×9

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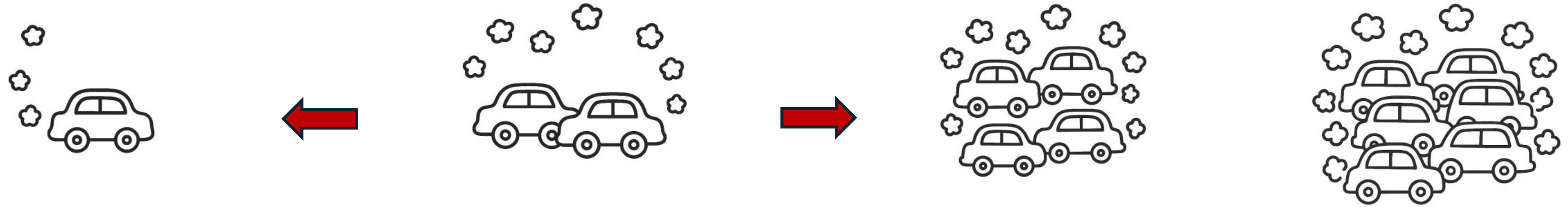

If [NO] is halved (×0.5) :
r decreases by 0.5^2 = ×0.25

If [NO] doubles (×2) :
r increases by 2^2 = ×4

If [NO] triples (×3) :
r increases by 3^2 = ×9

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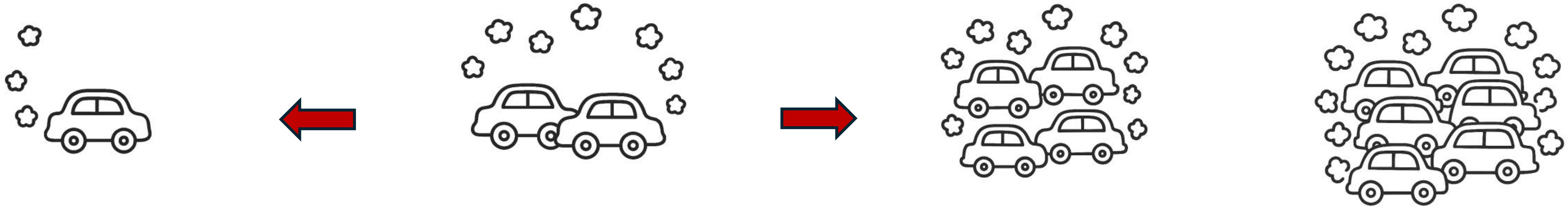

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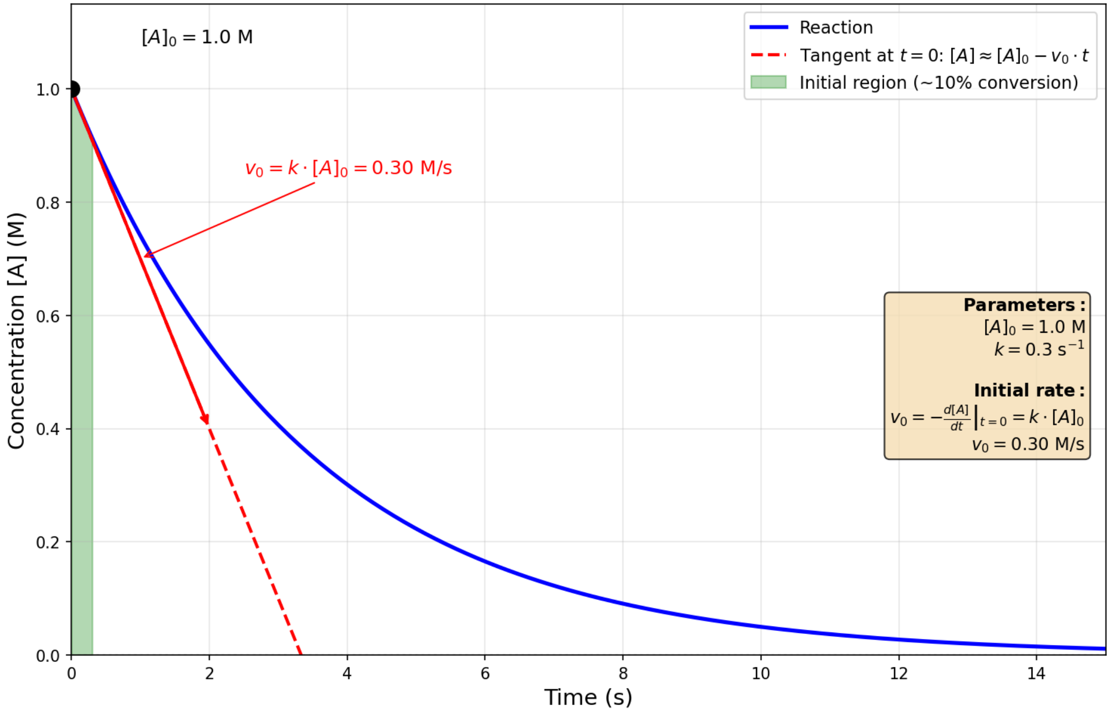
Any increase in traffic produces a disproportionately larger increase in smog formation rate.
But also, even a modest reduction in emissions has a significant impact on improving air quality.

The quest for an equation



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While we have an approximate method for determining kinetic parameters, we have yet to account for how concentration affects reaction rates (important to achieve exact results!).

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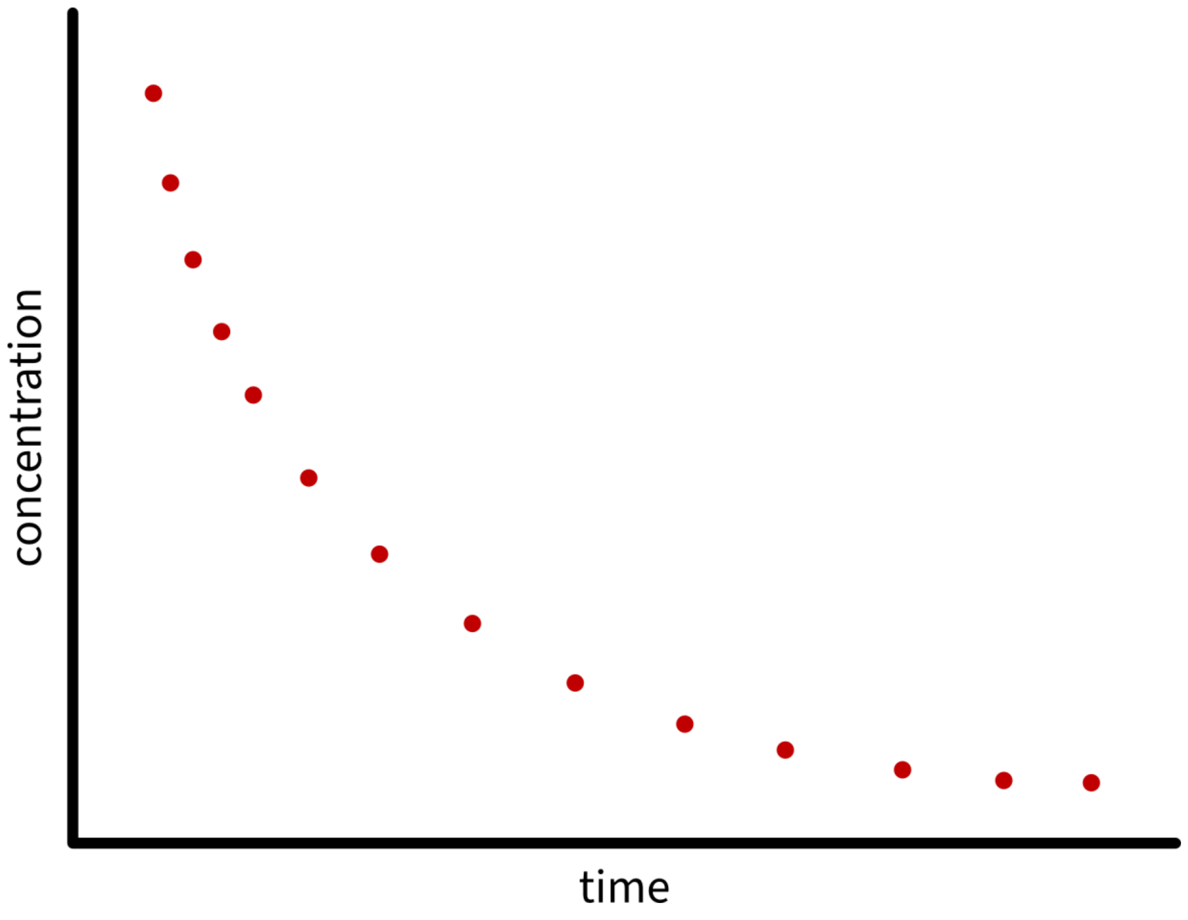

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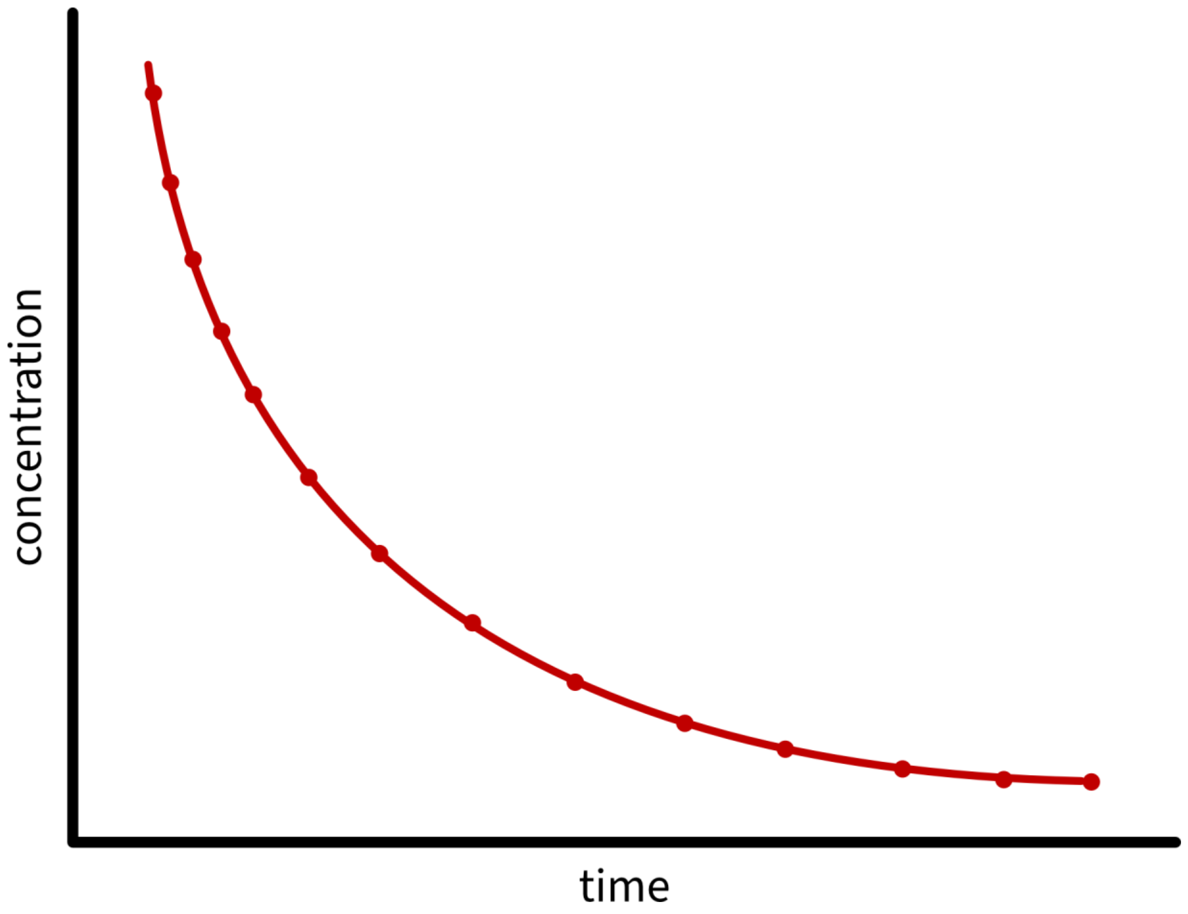

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Integrated Rate Law for a Second-Order Reaction

If a reaction is second order with respect to A, the rate at which A is consumed is proportional to the square of its concentration:

$$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2$$

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$$\frac{d}{dx}\left(x^n\right) = nx^{n-1}$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k\int_0^t dt \quad \Rightarrow \quad \frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0} = kt \quad \Rightarrow$$

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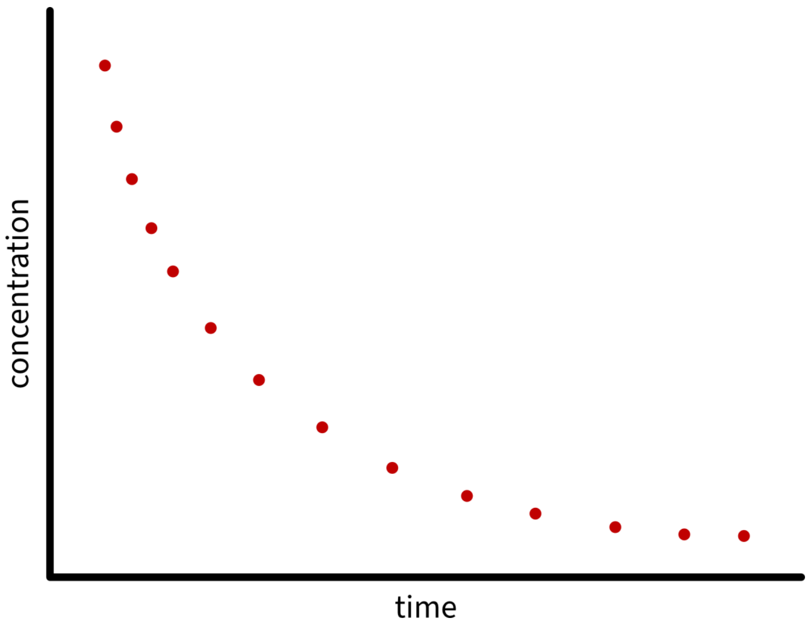
$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$

Integrated Rate Law for a Second-Order Reaction

the use

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$

The integrated rate law has a convenient linear form: $y = a + bx$.
By plotting the inverse of the measured concentration, the data become linear, allowing the parameters to be extracted from the slope and intercept!



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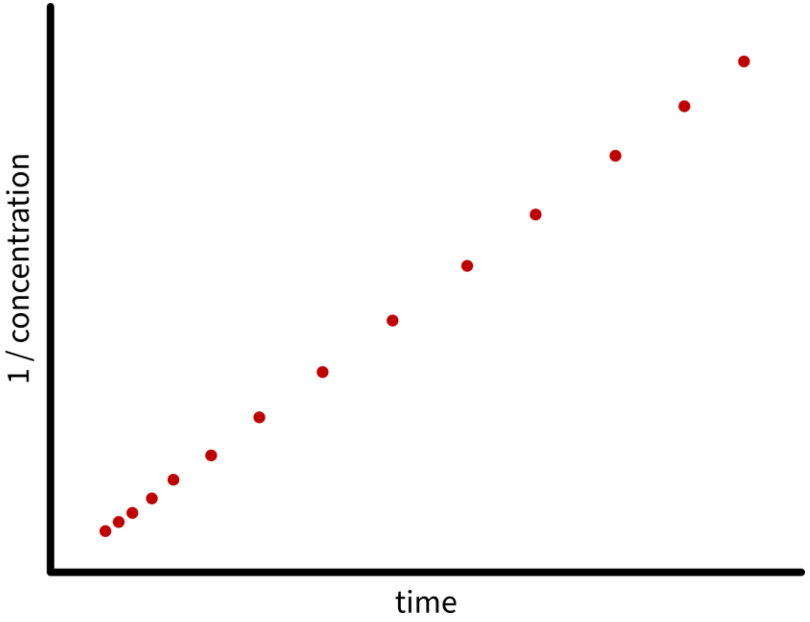

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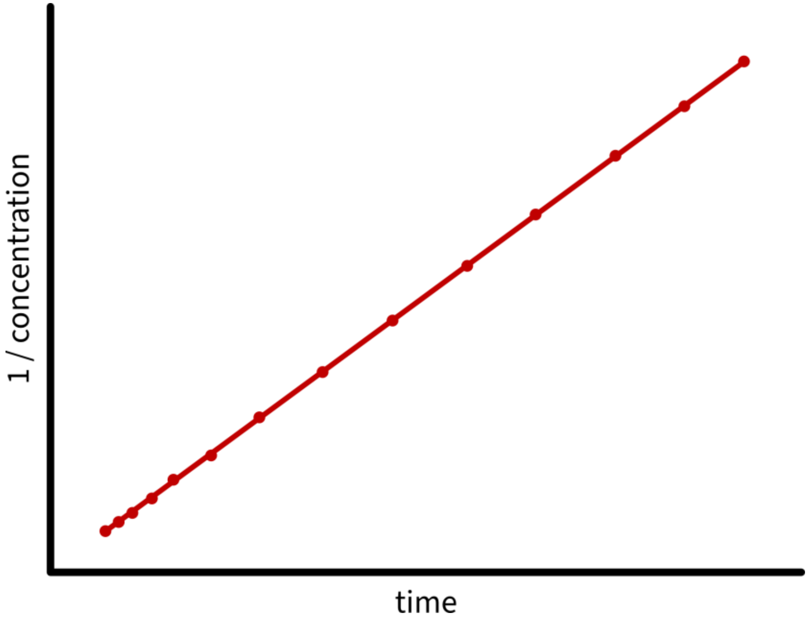


Exercise

Nitrogen dioxide (NO_2) is a reddish-brown gas and a major air pollutant. At high temperatures, NO2 decomposes into nitric oxide (NO) and oxygen:

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

The decomposition follows second-order kinetics with respect to NO_2. A research team studying combustion exhaust measured the concentration of NO_2 over time at 650 K:

Time (s)	$[NO_2]$ (mol/L)
0	1.00×10^{-2}
50	6.25×10^{-3}
100	4.55×10^{-3}
150	3.57×10^{-3}
200	2.94×10^{-3}
300	2.17×10^{-3}
400	1.72×10^{-3}

Verify the reaction order and determine the rate constant

Exercise

As they already told that the reaction is second order overall, we calculate directly the inverse of the concentration with time:

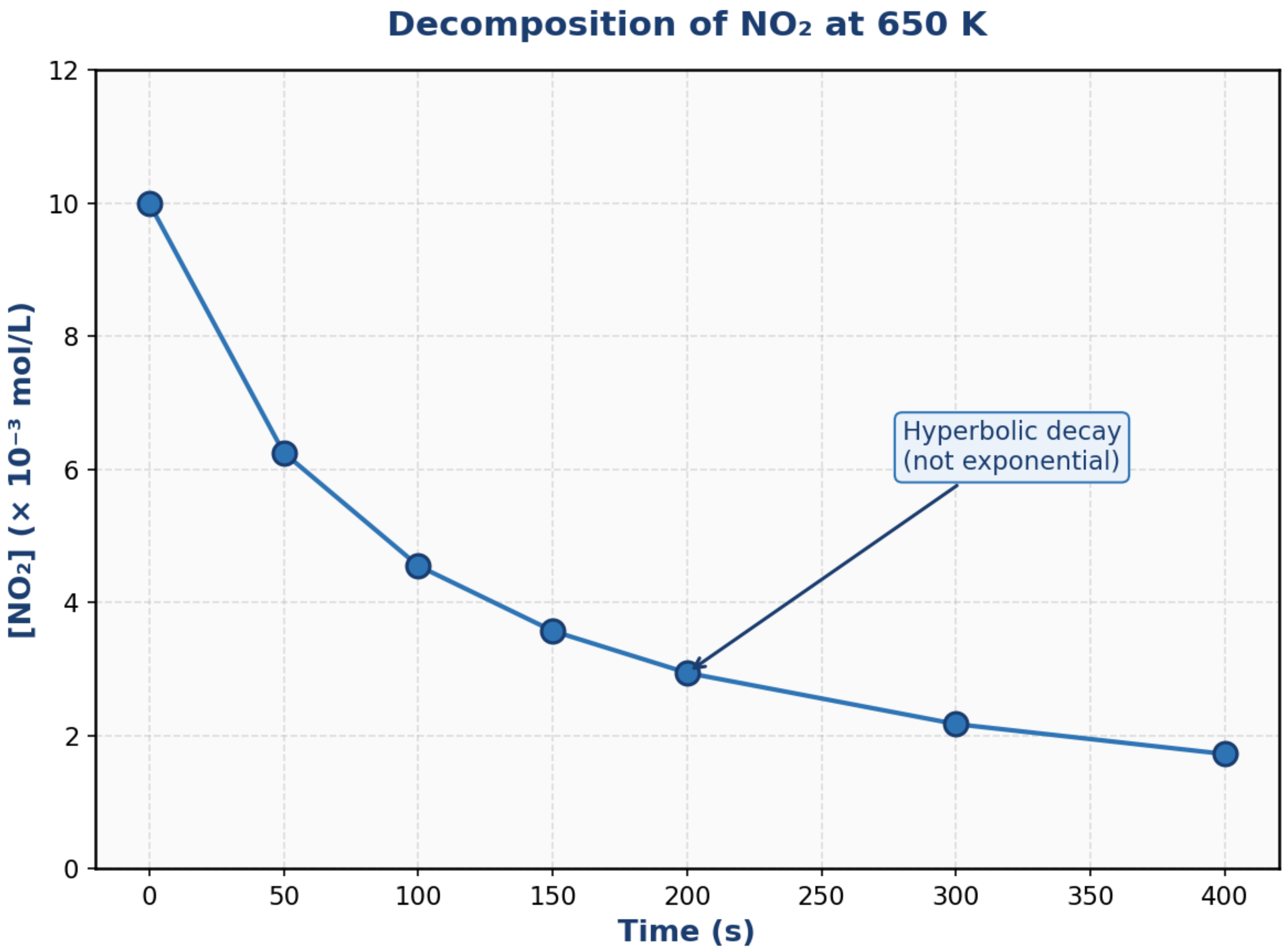
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Time (s)	$[NO_2]$ (mol/L)	1/ $[NO_2]$ (L/ mol)
0	1.00×10^{-2}	100
50	6.25×10^{-3}	160
100	4.55×10^{-3}	220
150	3.57×10^{-3}	267
200	2.94×10^{-3}	340
300	2.17×10^{-3}	460
400	1.72×10^{-3}	581

If the plot is linear, this confirms that the reaction is second order...

Exercise

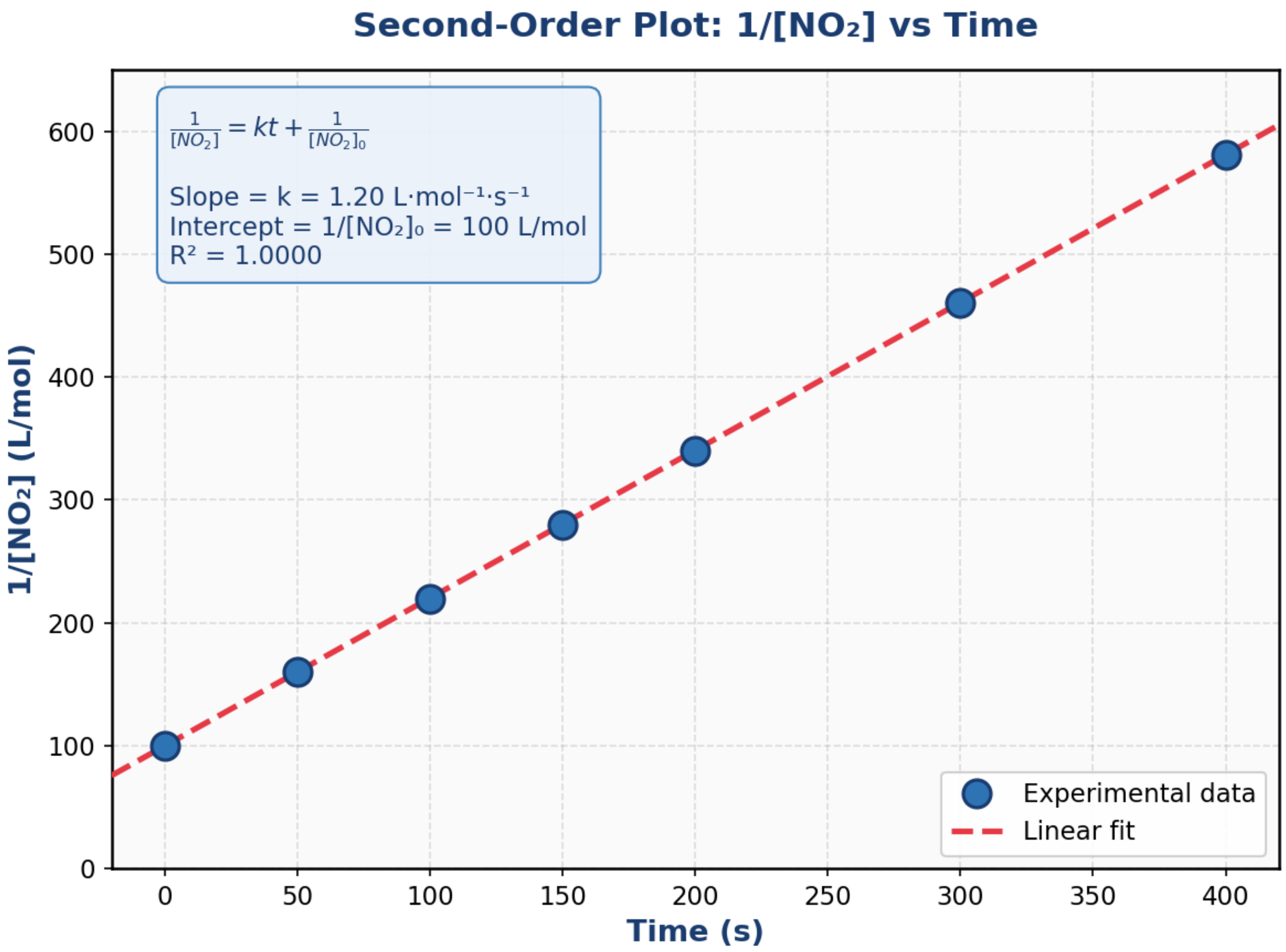
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$



Exercise

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

- It is confirmed that the reaction is second order.
- From the slope, we obtain a value of $k = 1.2\ \mathrm{M^{-1}\ s^{-1}}$.
- The intercept of the fitted line with the y-axis further confirms the consistency of the analysis.



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We solve the ordinary differential equation…

$$\frac{d}{dx}(\ln x) = \frac{1}{x}$$

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k\,dt \quad \Rightarrow \quad \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k \int_0^t dt' \quad \Rightarrow \quad \ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \quad \Rightarrow$$

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et voilà!

⚠

$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{-kt}$$

Integrated Rate Law for a First-Order Reaction

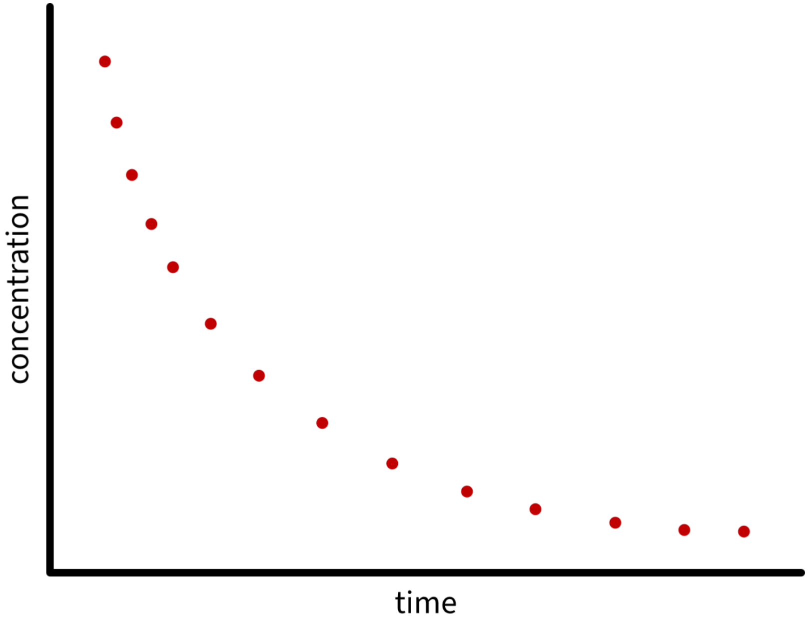
the use

⚠

$$[A] = [A]_0\, e^{-kt}$$

This time, the equation isn't linear ($y = a + bx$). But don't worry, it's pretty easy to fix that! Just by taking natural logarithms:

$$\Rightarrow \quad \ln{[A]} = \ln[A]_0 - kt$$



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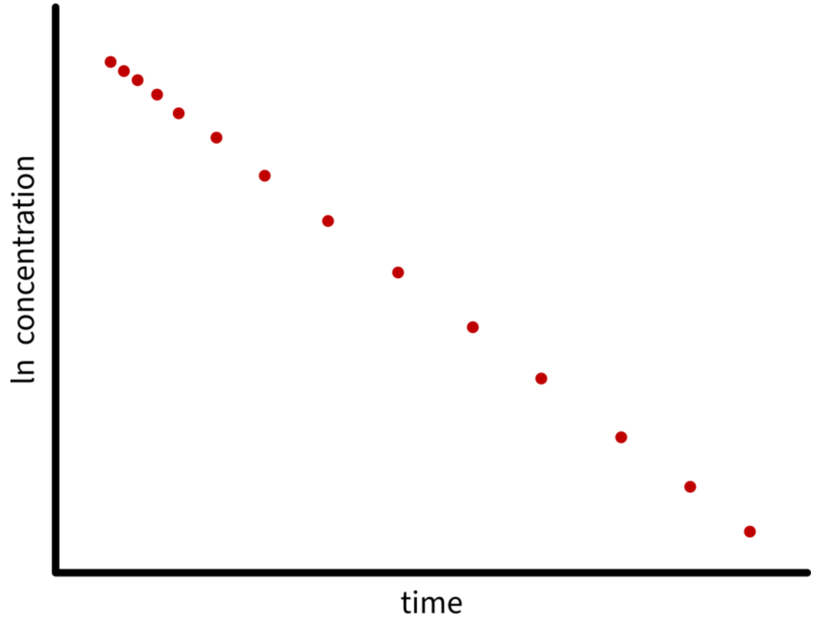

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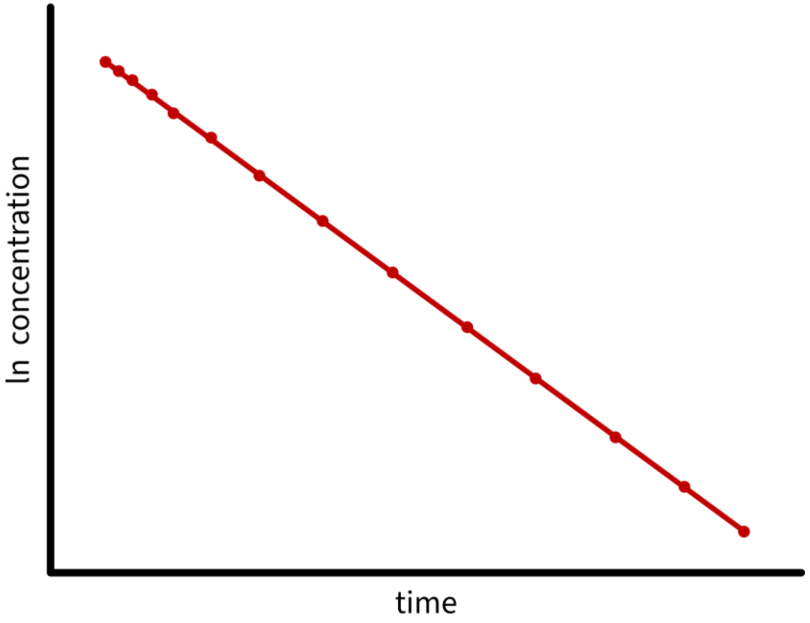

Integrated Rate Law for a Zero-Order Reaction

If a reaction is zeroth order with respect to A, the rate at which A is consumed is independent (!) to its concentration:

$$r = -\frac{d[\mathrm{A}]}{dt} = k$$

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We solve the ordinary differential equation…

$$d[\mathrm{A}] = -k\,dt \quad \Rightarrow \quad \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} d[\mathrm{A}] = -k\int_0^t dt' \quad \Rightarrow \quad [\mathrm{A}] - [\mathrm{A}]_0 = -kt \quad \Rightarrow$$

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et voilà (encore une fois)!

⚠

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Integrated Rate Law for a Zero-Order Reaction

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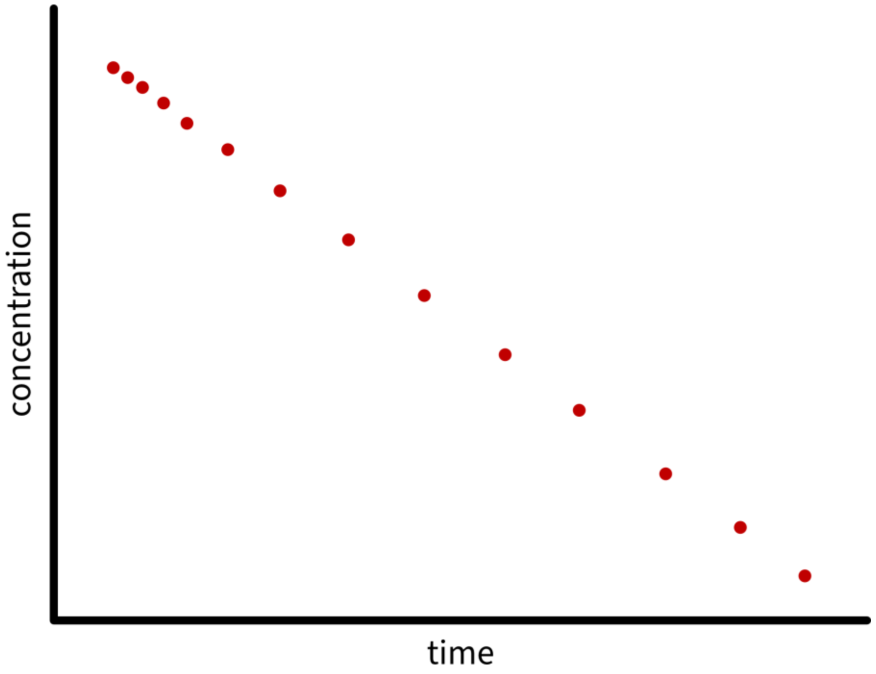
This time, the equation is already linear!!



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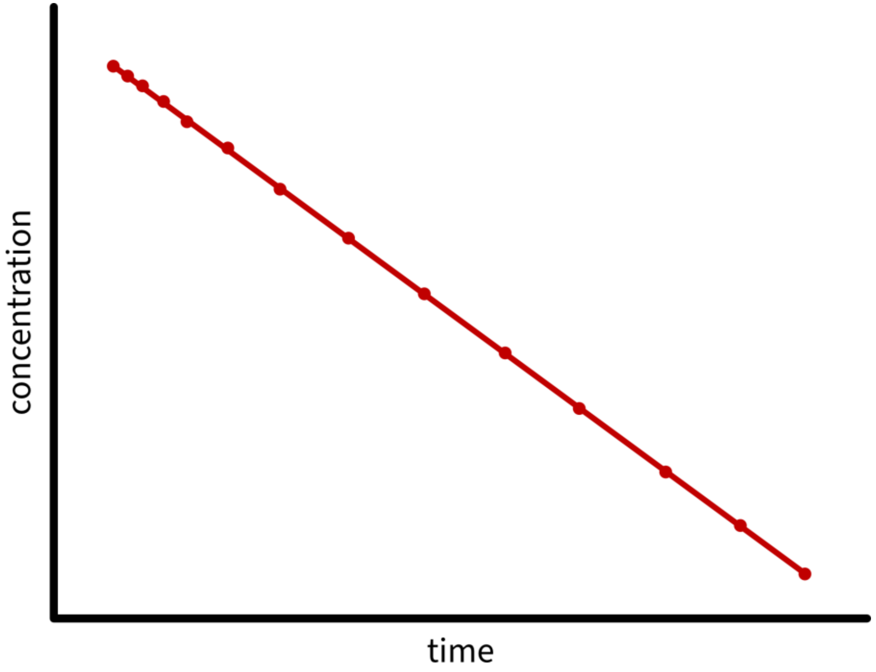
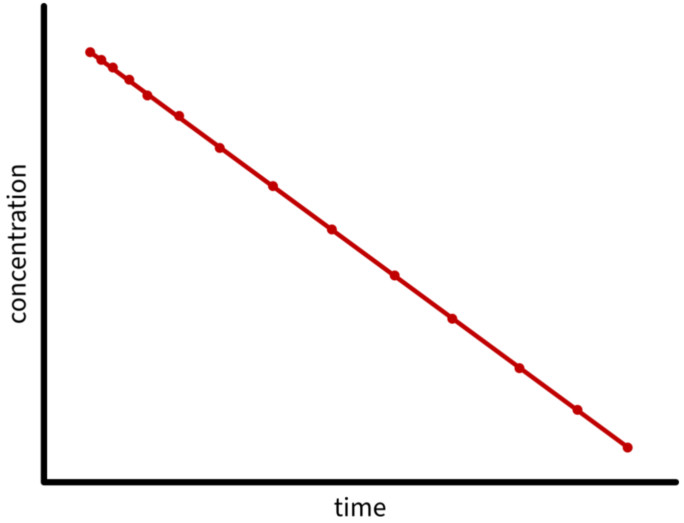


I don’t know how to do a linear regression, what can I do?

No *problemo*! You can still use the integral method to find the reaction order. It’s just a matter of figuring out which equation turns the data into a straight line.

Zero-order

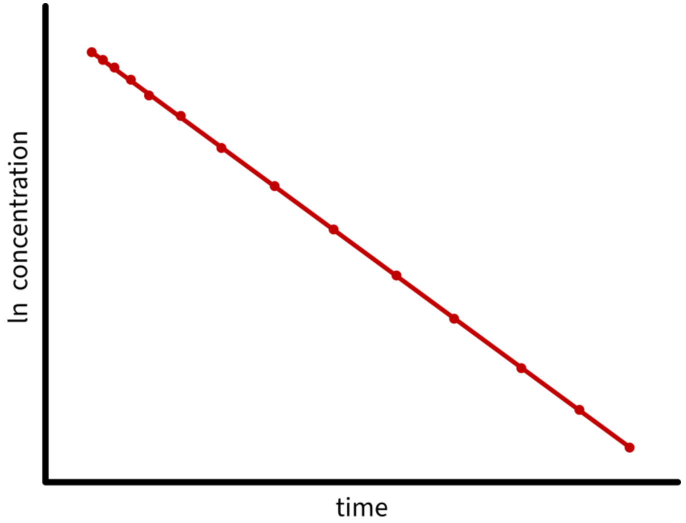
$$[\mathrm{A}] = [\mathrm{A}]_0 - kt$$



[A] vs t

First-order

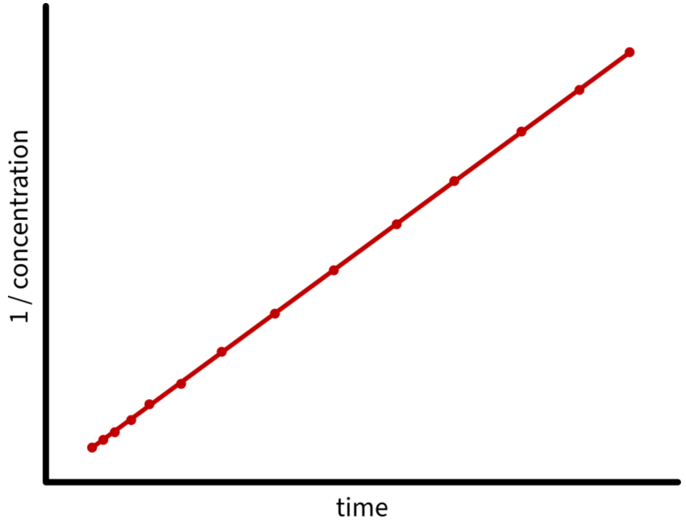
$$[\mathrm{A}] = [\mathrm{A}]_0 \, e^{-kt}$$



ln [A] vs t

Second-order

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$



1/[A] vs t

Exercise

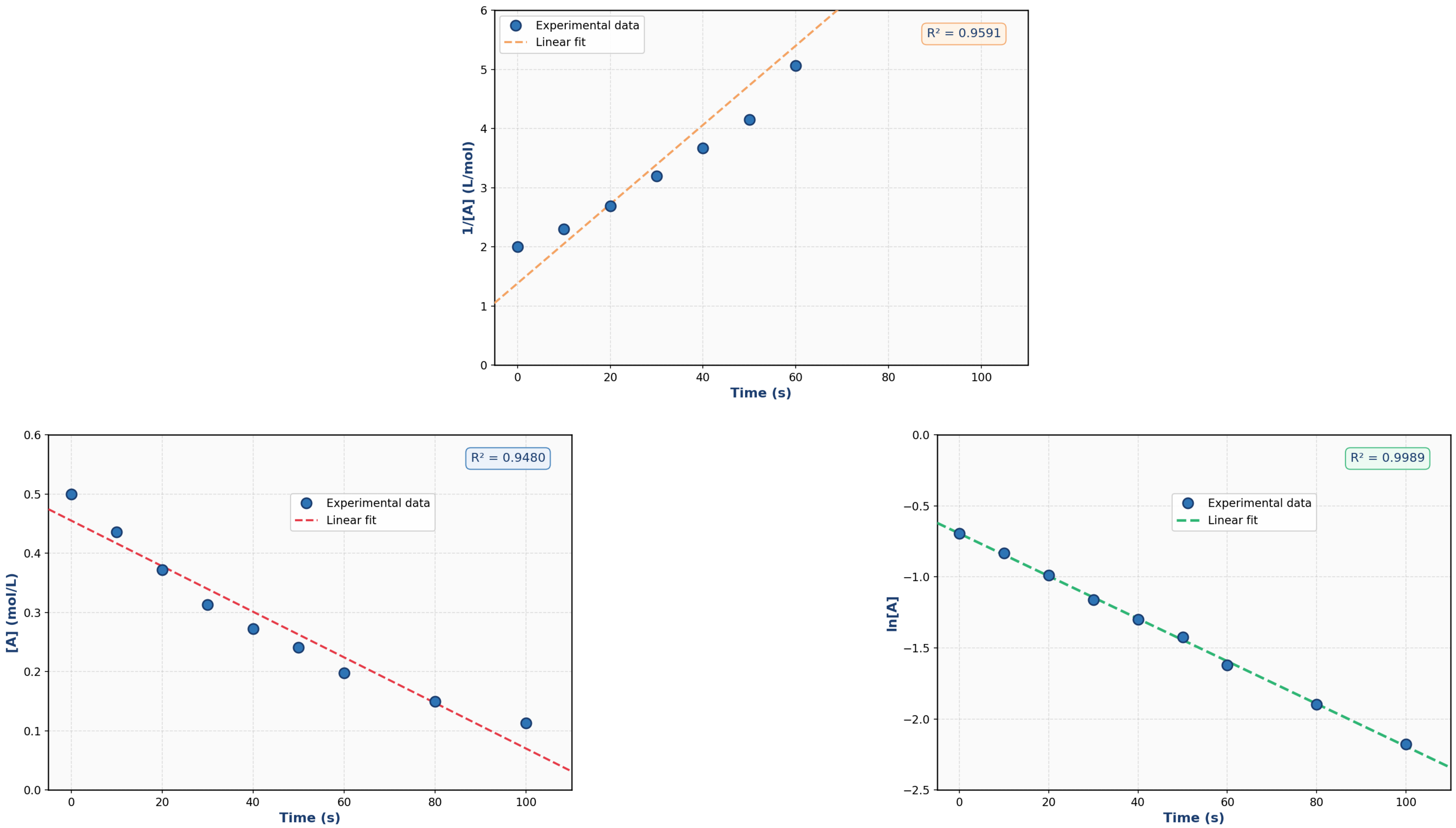
A Scottish chemist is studying the decomposition of a compound A in solution at 25°C.

$$\mathrm{A} \longrightarrow \mathrm{Products}$$

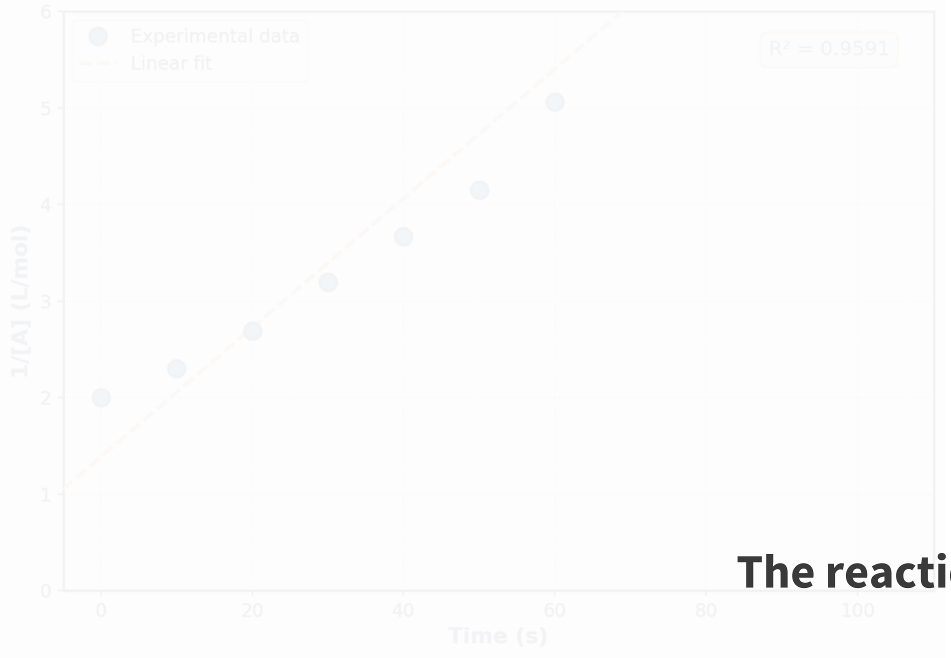
The concentration of A was measured at various times, yielding the following data:

Time (s)	[A] (mol/L)
0	0.500
10	0.436
20	0.372
30	0.313
40	0.273
50	0.241
60	0.197
80	0.150
100	0.113

Determine the reaction order.



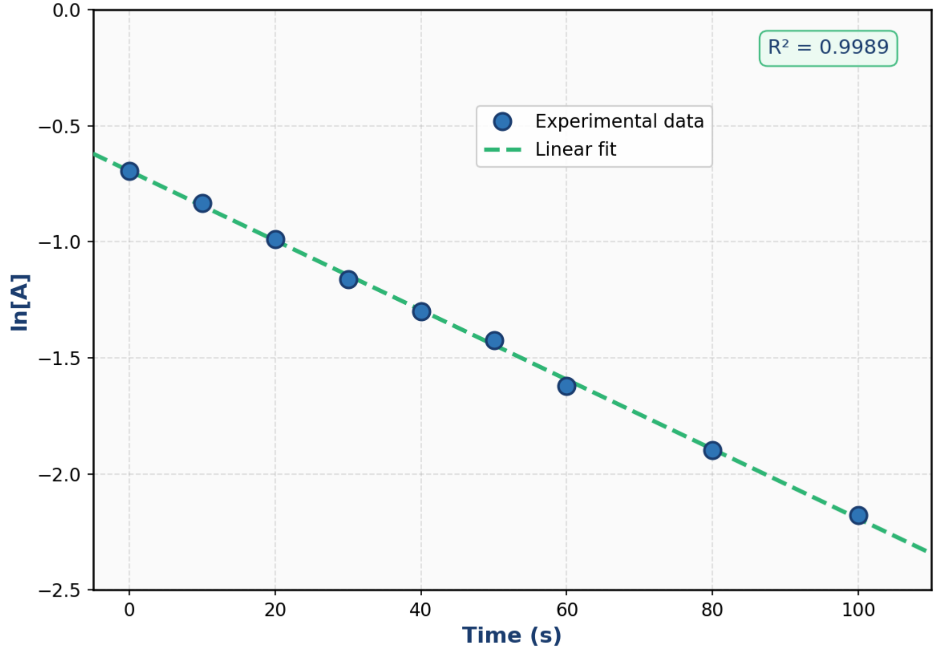
Experimental data
Linear fit
R² = 0.9591
1/[A] (L/mol)
Time (s)
Experimental data
Linear fit
R² = 0.9480
[A] (mol/L)
Time (s)
Experimental data
Linear fit
R² = 0.9989
ln[A]
Time (s)



$$\mathrm{A} \longrightarrow \text{Products}$$

$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{-kt}$$

The reaction is first order with respect to A



Exercise

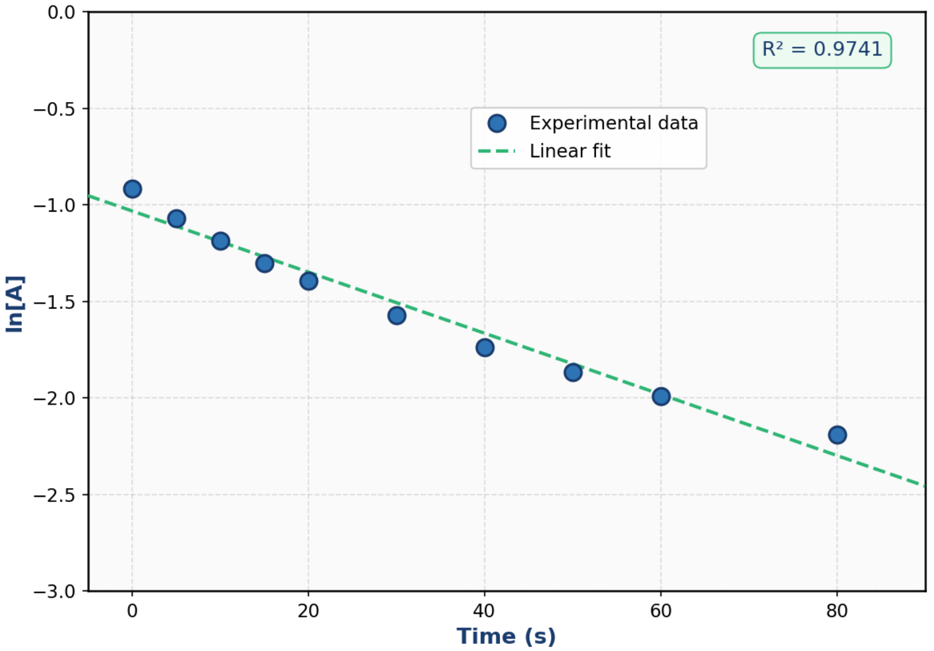
The dimerization of butadiene (C_4H_6) in the gas phase at 500 K was studied:

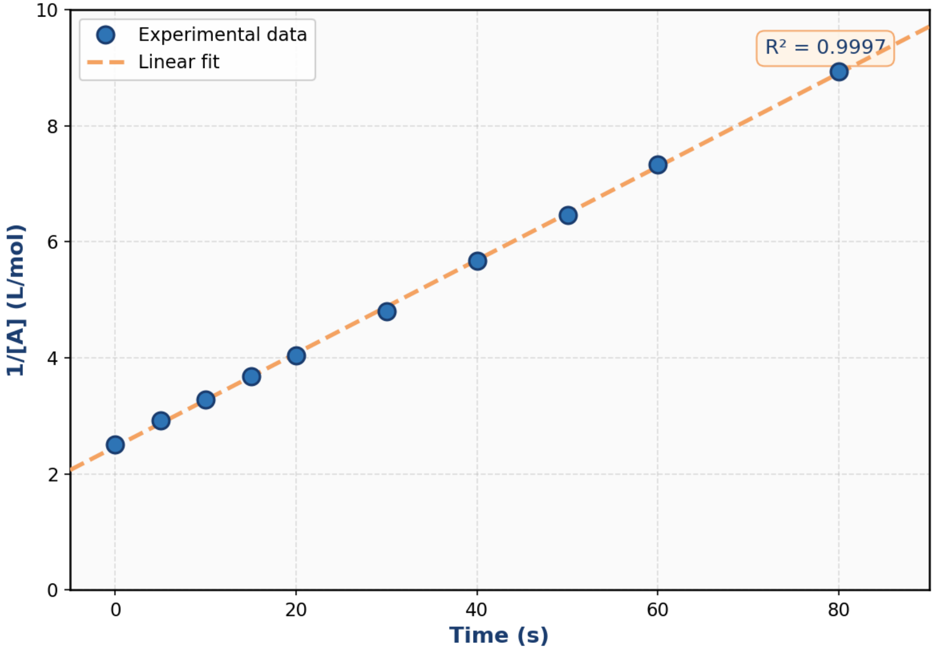
$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

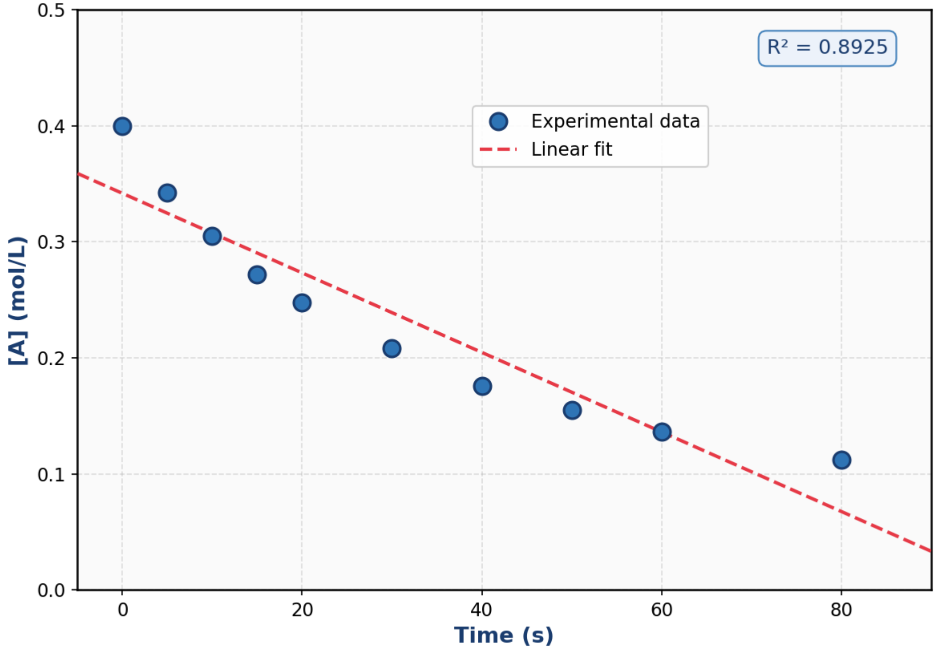
The concentration of butadiene was measured over time, yielding the following data:

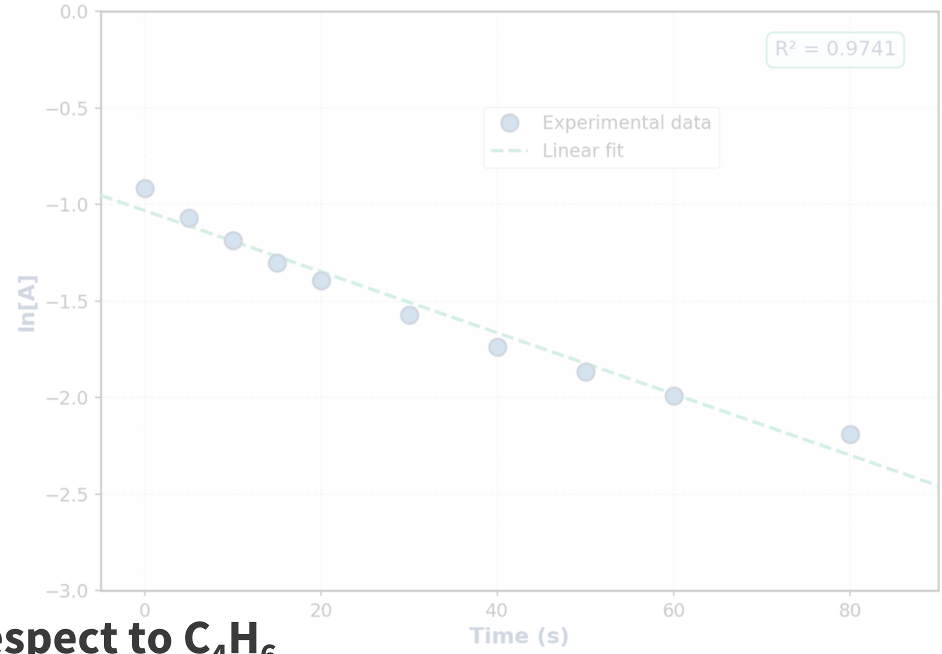
Time (s)	$[C_4H_6]$ (mol/L)
0	0.400
5	0.343
10	0.305
15	0.272
20	0.248
30	0.208
40	0.176
50	0.155
60	0.136

Determine the reaction order.

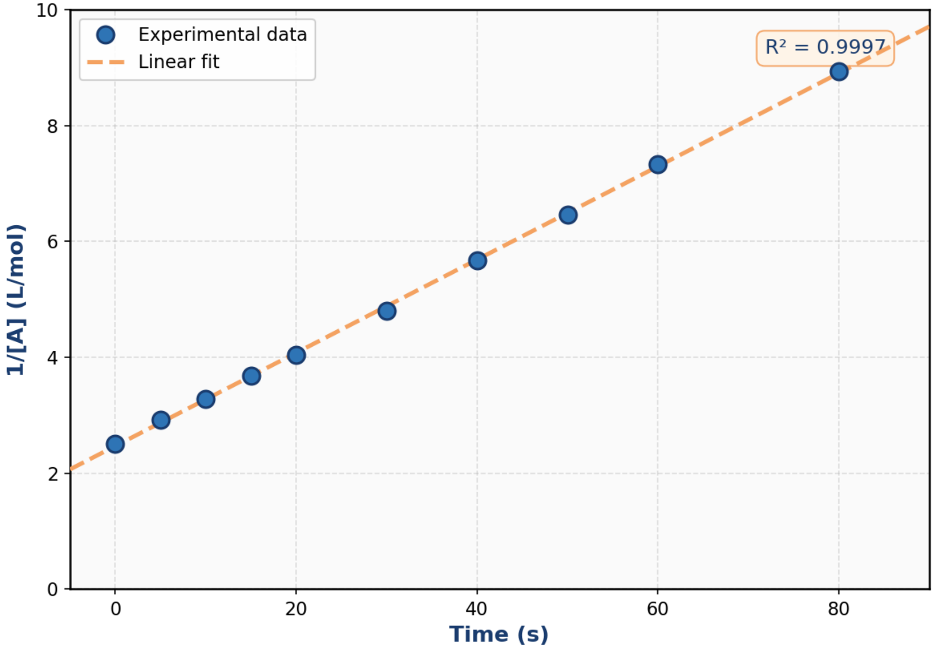

R² = 0.9741
Experimental data
Linear fit
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
ln[A]
0
20
40
60
80
Time (s)


Experimental data
Linear fit
R² = 0.9997
10
8
6
4
2
0
1/[A] (L/mol)
0
20
40
60
80
Time (s)


R² = 0.8925
Experimental data
Linear fit
0.5
0.4
0.3
0.2
0.1
0.0
[A] (mol/L)
0
20
40
60
80
Time (s)



The reaction is second order with respect to C_4H_6



Two Reactants, No Problem: the Isolation Method

$$-\frac{d[A]}{dt} = k[A]^2[B]^2$$

Two Reactants, No Problem: the Isolation Method

Sometimes, we can find complicated rate laws:

$$-\frac{d[A]}{dt} = k[A]^2[B]^2$$

This is the integrated equation:

$$\frac{1}{\Delta^3}\left[\ln\left(\frac{[A]+\Delta}{[A]}\right) + \frac{\Delta}{[A]+\Delta} - \frac{\Delta}{[A]} - \ln\left(\frac{[A]_0+\Delta}{[A]_0}\right) - \frac{\Delta}{[A]_0+\Delta} + \frac{\Delta}{[A]_0}\right] = kt$$

Where:

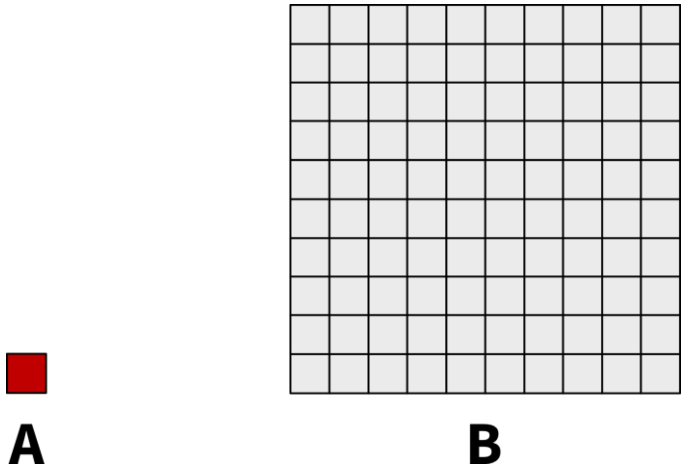
$$\Delta = [B]_0 - [A]_0$$

Two Reactants, No Problem: the Isolation Method

$$A + B \longrightarrow C$$

If one reactant is in large excess ([B] >>> [A]), its concentration barely changes during the reaction:

$$[B] \approx constant$$



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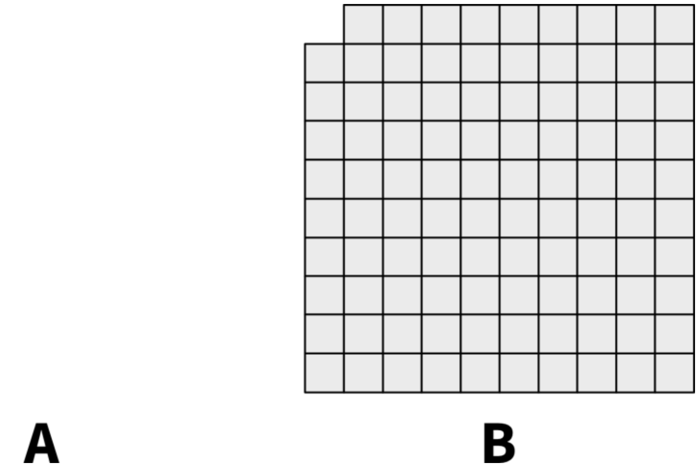

Two Reactants, No Problem: the Isolation Method

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

If one reactant is in large excess ([B] >>> [A]), its concentration barely changes during the reaction:

$$[B] \approx constant$$

and can therefore be incorporated into the rate constant!

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

where $k' = k[\mathrm{B}]^{\beta}$

If α=1, the reaction is referred to as a **pseudo–first-order reaction**.
If α=2, the reaction is referred to as a **pseudo–second-order reaction**.
and so on…

k says: This method can be used anytime we have a complex chemical reaction!

Challenge question

Ozone (O3) in the stratosphere protects life on Earth by absorbing harmful ultraviolet (UV) radiation from the Sun. Ozone naturally decomposes through a reaction with atomic oxygen:

$$O_3(g) + O(g) \rightarrow 2\,O_2(g)$$

Scottish researchers measured the initial rate of O_2 formation (r_0) at different concentrations of ozone [O_3] and atomic oxygen [O] at 250 K:

Exp.	[O_3] (M)	[O] (M)	r_0 (M/s)
1	1.0×10^{-5}	1.0×10^{-8}	4.8×10^{-4}
2	2.0×10^{-5}	1.0×10^{-8}	9.6×10^{-4}
3	1.0×10^{-5}	2.0×10^{-8}	9.6×10^{-4}
4	3.0×10^{-5}	1.0×10^{-8}	1.44×10^{-3}

Part A

a) Determine the order with respect to ozone [O_3].
b) Determine the order with respect to atomic oxygen [O].
c) Write the complete rate law for this reaction.
d) Calculate the rate constant *k* and express it with the correct units.

Challenge question

Part B

In a separate set of experiments, the researchers used a large excess of ozone ($[O_3] = 5.0 \times 10^{-4}$ M) and varied only the atomic oxygen concentration:

Exp.	[O] (M)	r_0 (M/s)
1	2.0×10^{-9}	4.8×10^{-3}
2	4.0×10^{-9}	9.6×10^{-3}
3	6.0×10^{-9}	1.44×10^{-2}
4	8.0×10^{-9}	1.92×10^{-2}

a) Explain why $[O_3]$ can be considered constant in these experiments.
b) Write the pseudo-order rate law under these conditions.
c) Calculate the rate constant *k*' and express it with the correct units.
d) Calculate the true rate constant *k* and express it with the correct units.