SciFun

Chemical Kinetics – 4

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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.

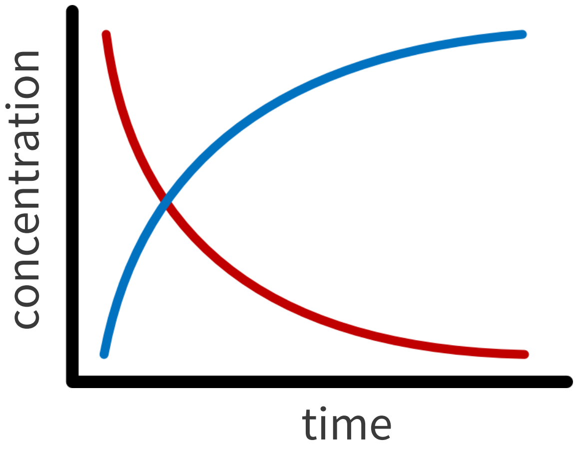
Beer law

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

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

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



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

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

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

Exercise

Show that the units of the rate constant for reactions of different orders are as follows:

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

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The units of the reaction rate are always:

$$r \quad (\mathrm{M\ s^{-1}})$$

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Order 3

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

The units of the reaction rate are always:

$r \quad (\mathrm{M\ s^{-1}})$

And the unit of concentration, which is the only quantity that changes, is:

$[\mathrm{A}] \quad (\mathrm{M})$

Exercise

Show that the units of the rate constant for reactions of different orders are as follows:

Order 0	Order 1	Order 2	Order 3
$\frac{r}{[\mathrm{A}]^0} = k$ (M s^{-1})	$\frac{r}{[\mathrm{A}]} = k$ (s^{-1})	$\frac{r}{[\mathrm{A}][\mathrm{B}]} = k$ (M^{-1} s^{-1})	$\frac{r}{[\mathrm{A}][\mathrm{B}]^2} = k$ (M^{-2} s^{-1})

The units of the reaction rate are always:

r (M s^{-1})

And the unit of concentration, which is the only quantity that changes, is:

$[\mathrm{A}]$ (M)

Therefore…

Exercise

Show that the units of the rate constant for reactions of different orders are as follows:

Order 0

$$\frac{r}{[\mathrm{A}]^0} = k$$

$$\left(\frac{\mathrm{M\ s^{-1}}}{\mathrm{M^0}}\right) = \left(\frac{\mathrm{M\ s^{-1}}}{1}\right) = \mathrm{M\ s^{-1}}$$

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Order 1

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

$$\left(\frac{\mathrm{M\ s^{-1}}}{\mathrm{M}}\right) = \mathrm{s^{-1}}$$

Exercise

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$$\left(\frac{\mathrm{M\ s^{-1}}}{\mathrm{M}^2}\right) = \left(\frac{\mathrm{s^{-1}}}{\mathrm{M^{-1}}}\right) = \mathrm{M^{-1}s^{-1}}$$

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$$\left(\frac{\mathrm{M\ s^{-1}}}{\mathrm{M^2}}\right) = \left(\frac{\mathrm{s^{-1}}}{\mathrm{M^{-1}}}\right) = \mathrm{M^{-1}s^{-1}}$$

Order 3

$$\frac{r}{[\mathrm{A}][\mathrm{B}]^2} = k$$

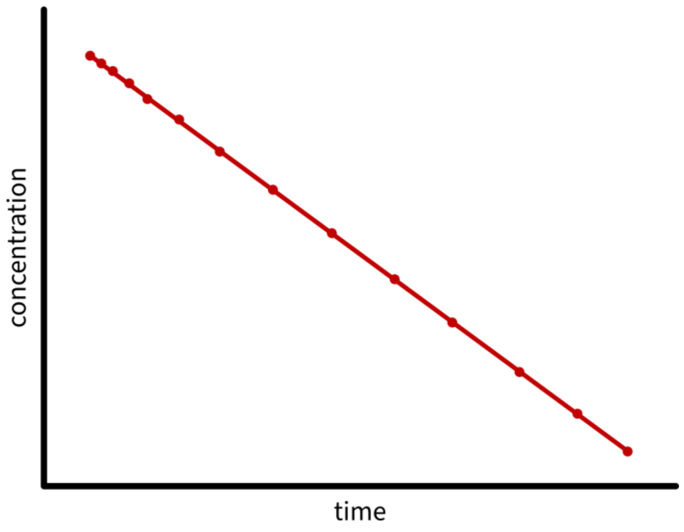
$$\left(\frac{\mathrm{M\ s^{-1}}}{\mathrm{M^3}}\right) = \left(\frac{\mathrm{s^{-1}}}{\mathrm{M^{-2}}}\right) = \mathrm{M^{-2}s^{-1}}$$

Previously on Chemical Kinetics...

The integral method determines the reaction order and rate constant by fitting concentration–time data to integrated rate laws

Zero-order

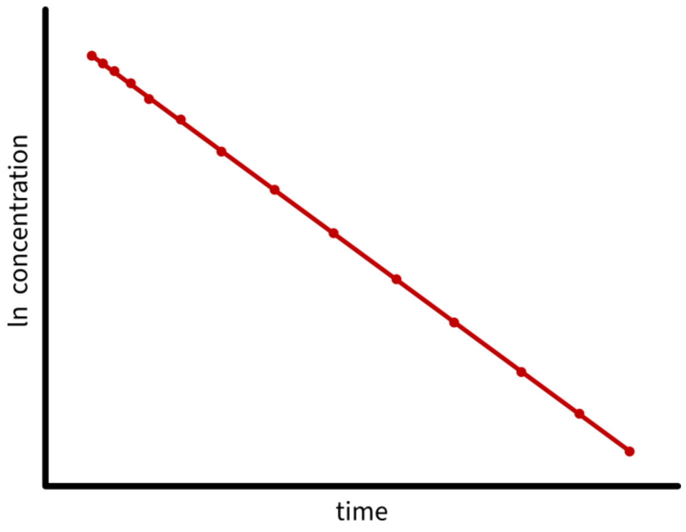
$$[A] = [A]_0 - kt$$



[A] vs t

First-order

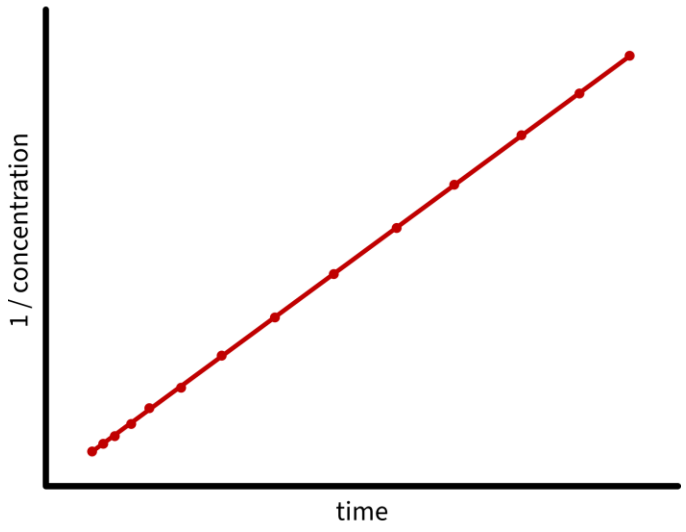
$$[A] = [A]_0\, e^{-kt}$$



ln [A] vs t

Second-order

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



1/[A] vs t

Exercise

The decomposition of ammonia (NH_3) on a hot tungsten (W) surface is studied:

$$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g) \qquad \text{(on W surface at 1100 °C)}$$

The concentration of ammonia was measured over time:

Time (s)	[A] (mol/L)
0	0.500
10	0.453
20	0.412
30	0.369
40	0.320
50	0.272
60	0.230
70	0.183
80	0.137
90	0.098

Determine the reaction order

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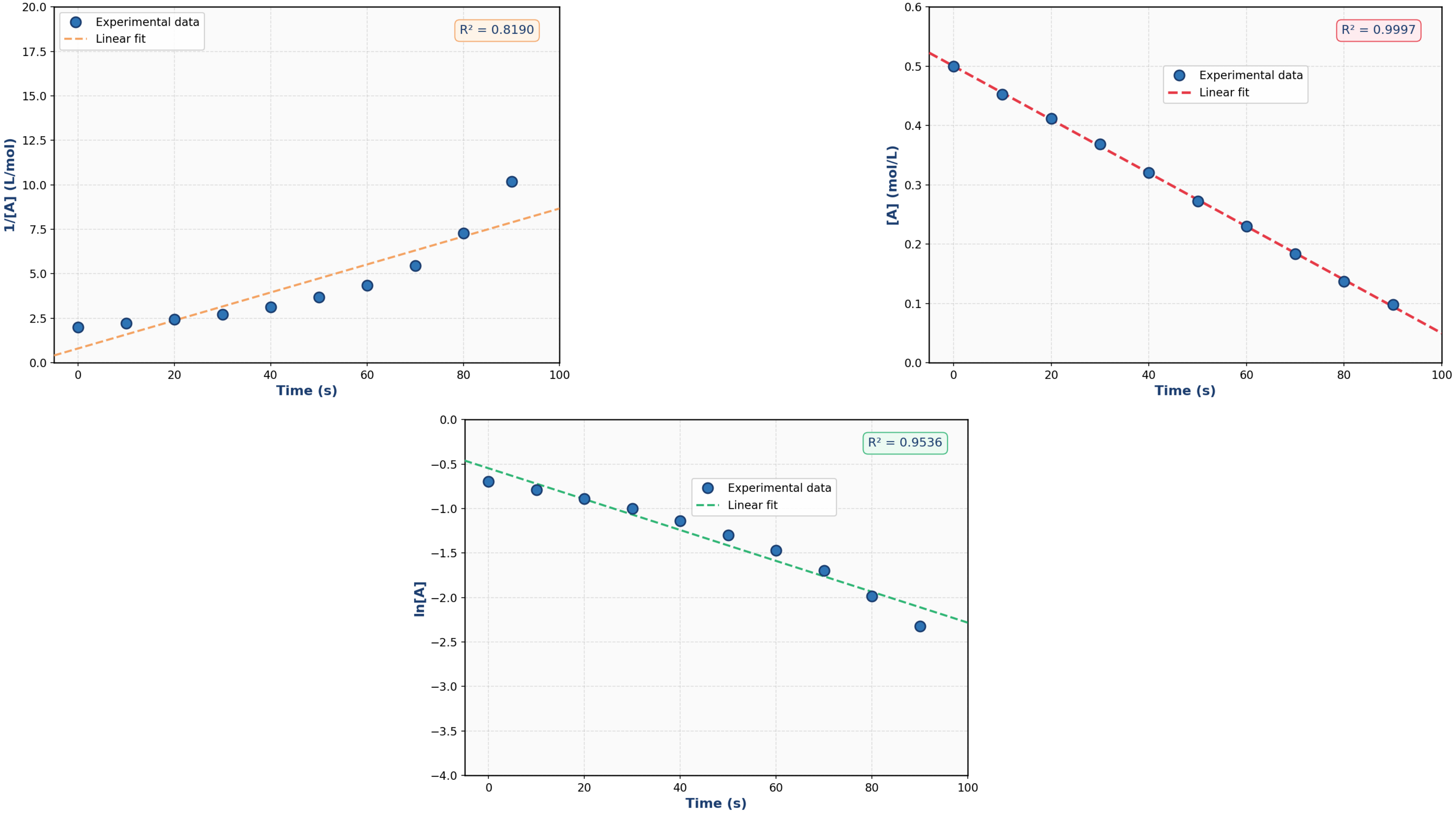
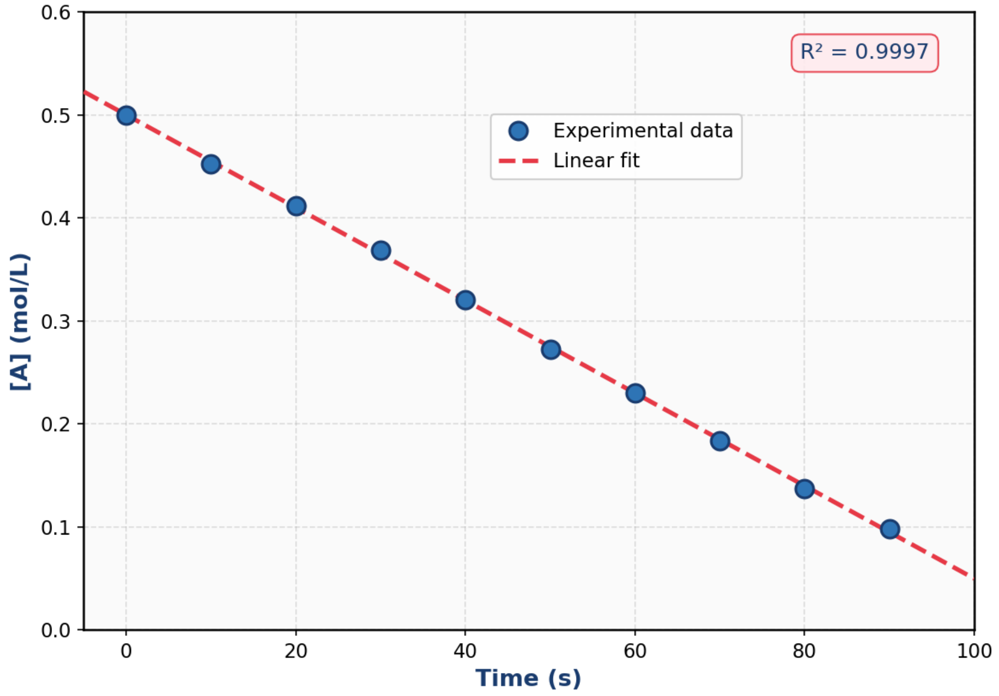
The concentration of ammonia was measured over time:

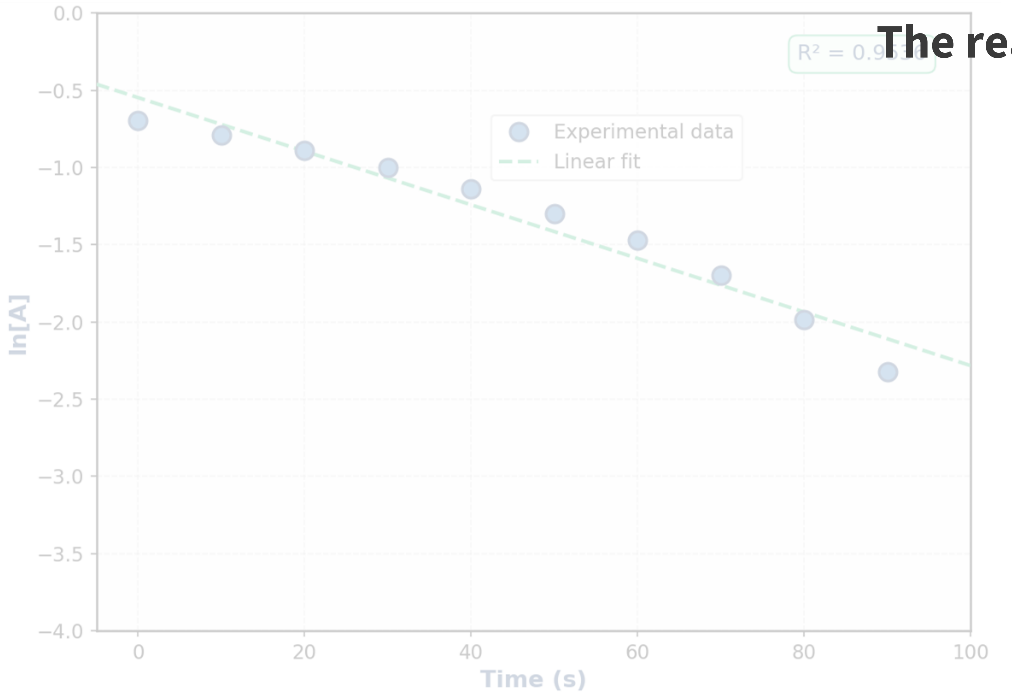
Time (s)	[A] (mol/L)	ln[A]	1/[A] (L/mol)
0	0.500	−0.693	2.00
10	0.453	−0.792	2.21
20	0.412	−0.888	2.43
30	0.369	−0.998	2.71
40	0.320	−1.139	3.12
50	0.272	−1.302	3.68
60	0.230	−1.469	4.34
70	0.183	−1.697	5.46
80	0.137	−1.986	7.29
90	0.098	−2.321	10.19

Determine the reaction order



R² = 0.8190
Experimental data
Linear fit
1/[A] (L/mol)
Time (s)
R² = 0.9997
Experimental data
Linear fit
[A] (mol/L)
Time (s)
R² = 0.9536
Experimental data
Linear fit
ln[A]
Time (s)

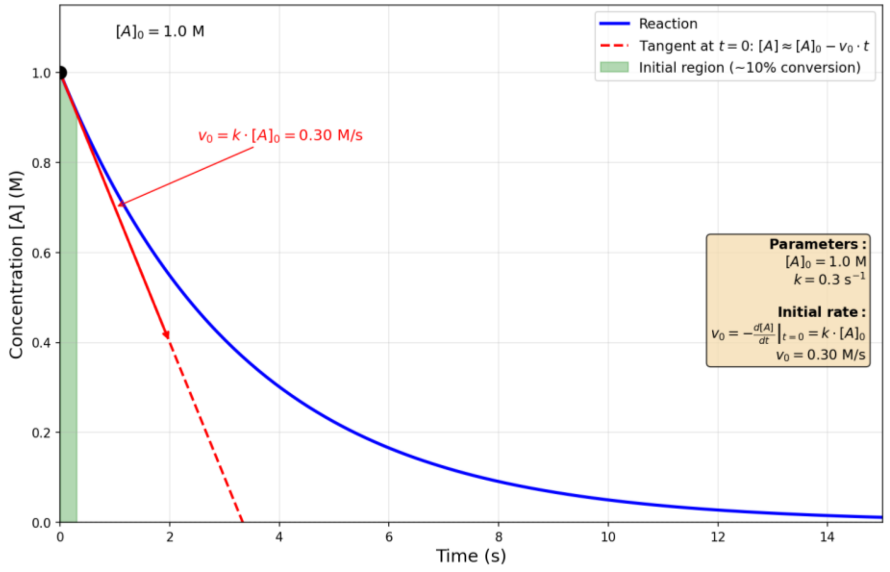




The reaction is zero-order with respect to A

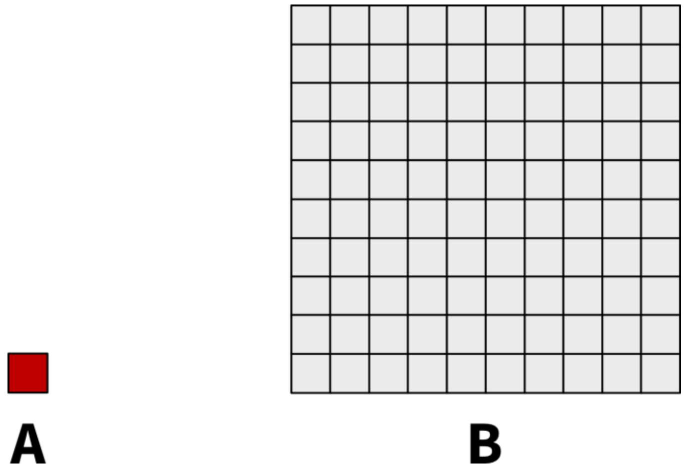
Previously on Chemical Kinetics...

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.



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

The isolation method determines the reaction order by keeping all but one reactant in large excess so their concentrations remain effectively constant, reducing the rate law to a pseudo-order form.



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

where:

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

Challenge question

Ozone (O_3) 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.

Part A

a) Determine the order with respect to ozone [O_3]

First, we define the rate law for the reaction:

$$r = k[\mathrm{O_3}]^{\alpha}[\mathrm{O}]^{\beta}$$

Comparing experiments 1 and 2 (where $[\mathrm{O}]_1^{\beta} = [\mathrm{O}]_2^{\beta}$ = 1.0 × 10^{-8} M is constant):

$$\frac{r_2}{r_1} = \left(\frac{[\mathrm{O_3}]_2}{[\mathrm{O_3}]_1}\right)^{\alpha}$$

Solving for α:

$$\frac{9.6 \times 10^{-4}\ \mathrm{M \cdot s^{-1}}}{4.8 \times 10^{-4}\ \mathrm{M \cdot s^{-1}}} = \left(\frac{2.0 \times 10^{-5}\ \mathrm{M}}{1.0 \times 10^{-5}\ \mathrm{M}}\right)^{\alpha}$$

$$2 = 2^{\alpha} \quad \Rightarrow \quad \alpha = 1$$

The reaction is first order with respect to O_3

b) Determine the order with respect to atomic oxygen [O]

The rate law for the reaction is now:

$$r = k[\mathrm{O_3}][\mathrm{O}]^{\beta}$$

Comparing experiments 1 and 3 (where $[\mathrm{O_3}]_1 = [\mathrm{O_3}]_3$ = 1.0 × 10^{-5} M is constant):

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

Solving for β:

$$\frac{9.6 \times 10^{-4}\ \mathrm{M \cdot s^{-1}}}{4.8 \times 10^{-4}\ \mathrm{M \cdot s^{-1}}} = \left(\frac{2.0 \times 10^{-5}\ \mathrm{M}}{1.0 \times 10^{-5}\ \mathrm{M}}\right)^{\beta}$$

$$2 = 2^{\beta} \quad \Rightarrow \quad \beta = 1$$

The reaction is first order with respect to O

c) Write the complete rate law for this reaction

$$r = k[O_3][O]$$

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

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

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

$$k = \frac{r}{[O_3][O]}$$

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

$$k = \frac{4.8 \times 10^{-4}\ \mathrm{M\ s^{-1}}}{1.0 \times 10^{-5}\ \mathrm{M} \cdot 1.0 \times 10^{-8}\ \mathrm{M}} \Rightarrow k = \frac{4.8 \times 10^{-4}\ \mathrm{M\ s^{-1}}}{1.0 \times 10^{-13}\ \mathrm{M^2}} \Rightarrow k = 4.8 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$$

Part B

a) Explain why $[O_3]$ can be considered constant in these experiments.

Because $[O_3] = 5.0 \times 10^{-4}$ M is approximately 10^5 times larger than [O] (10^{-9} M). Even if all the O atoms were to react, the change in $[O_3]$ would be negligible (< 0.01 %). Therefore, $[O_3] \approx [O_3]_0$ = constant throughout the experiment.

b) Write the pseudo-order rate law under these conditions.

$$r = k'[\text{O}]$$ where: $$k' = k[\text{O}_3]$$

c) Calculate the rate constant *k'* and express it with the correct units.

We isolate *k'* and then substitute using, for example, experiment 1:

$$k' = \frac{r}{[\text{O}]} \quad \Rightarrow \quad k' = \frac{4.8 \times 10^{-3}\ \text{M s}^{-1}}{2.0 \times 10^{-9}\ \text{M}} = 2.4 \times 10^{6}\ \text{s}^{-1}$$

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

$$k = \frac{k'}{[\text{O}_3]} \qquad k = \frac{2.4 \times 10^{6}\ \text{s}^{-1}}{5.0 \times 10^{-4}\ \text{M}} = 4.8 \times 10^{9}\ \text{M}^{-1}\ \text{s}^{-1}$$

The half-life of a first-order reaction

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

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

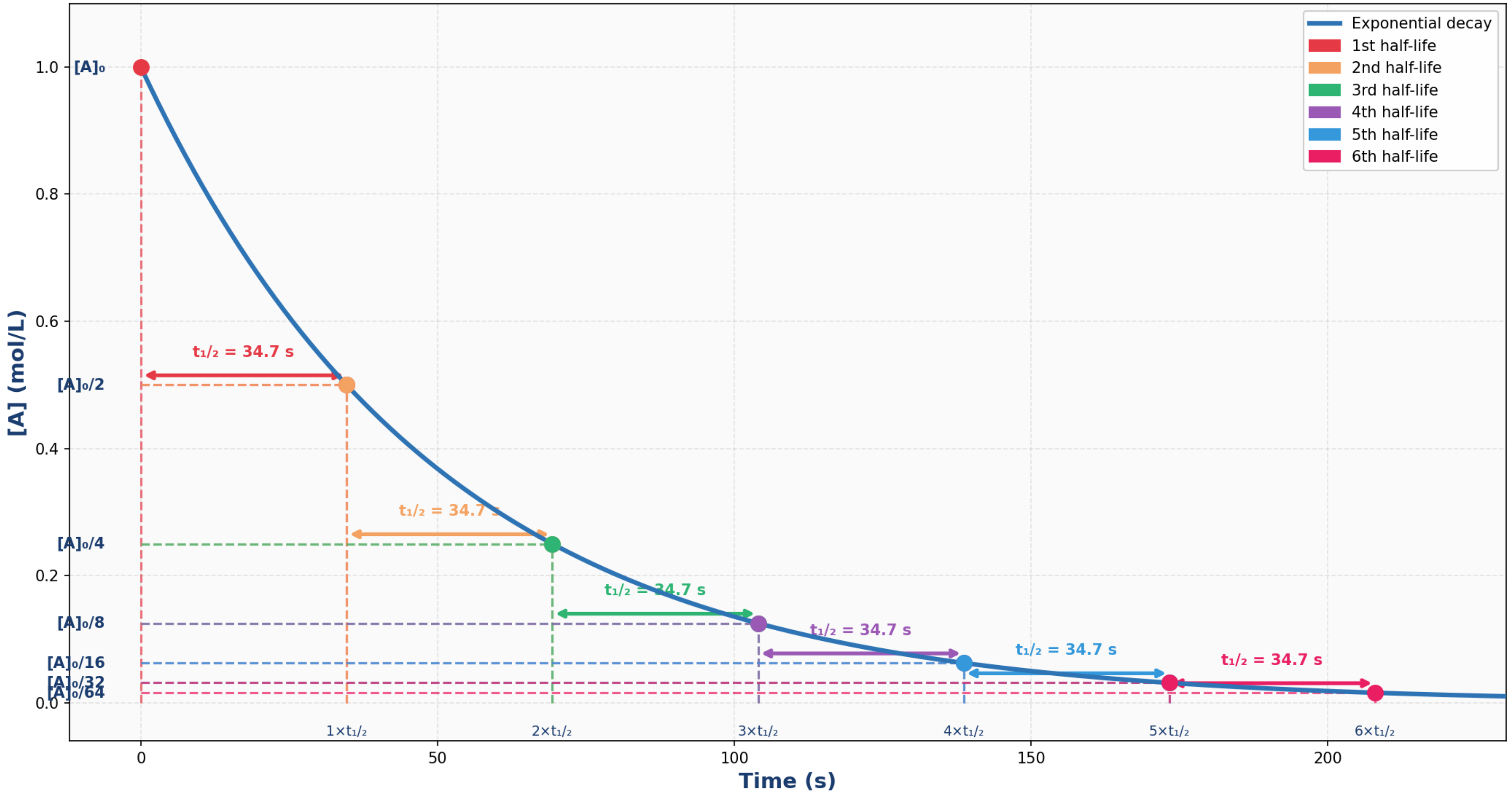
This is very interesting: This implies that the greater the amount of reactant present, the faster the reaction proceeds, but always in direct proportion. It does not matter how the system started or what happened before: the future behaviour depends only on its current value. That’s why is the favourite reaction in nature! It appears in:

- Unimolecular chemical reactions
- Radioactive decays
- Thermal relaxations
- Capacitor discharges
- Simple population (people) kinetics

And because of that, it is possible to describe the reaction with a single, very intuitive time: The half-life of the reaction!!

The half-life of a first-order reaction

The half-life, $t_{1/2}$, is simply the time it takes for the concentration to fall to half of its initial value, $[A]_{t1/2} = ½\ [A]_0$. And here's the cool part: because the reaction only 'cares' about its current value, this time is **always the same**, which makes it incredibly useful



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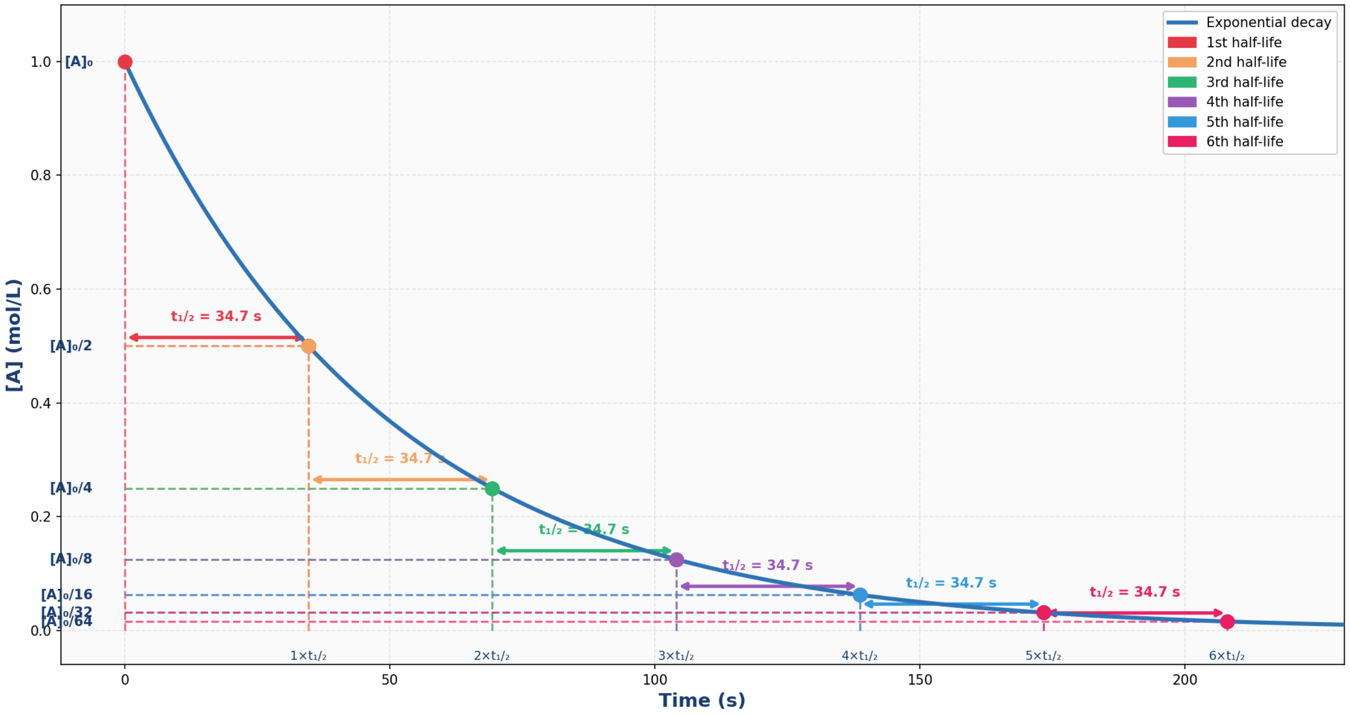

And it's super simple to calculate. You just need to check how long it takes for the reaction to reach half of its initial concentration:

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -kt_{1/2} \Rightarrow t_{1/2} = -\frac{\ln \frac{1}{2}}{k} = -\frac{\ln 1 - \ln 2}{k}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

(Note: it is inversely proportional to *k*)

Half-life: uses

Pharmacology: Determines how long a drug remains active in the body, which in turn defines the dosing frequency. A medication with a $t_1/_2$ of 4 hours needs to be taken several times a day, whereas one with a $t_1/_2$ of 24 hours is taken once daily.

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Exercise

Jamie, a 70 kg UofG's student, attends a party in the Southside on Saturday evening. Over the course of 2 hours (from 8 PM to 10 PM), Jamie drinks 4 pints of beer (approximately 8 units of alcohol). By 10 PM, when Jamie stops drinking, their BAC (Blood alcohol content) has reached a peak of 0.16%. Given that alcohol elimination follows a first-order kinetics with a half-life in its body of $t_{1/2}$ = 4.5 hours* and Jamie needs to drive home to the west end, at what time will Jamie be able to drive back home?

Note: The current drink drive limit in Scotland is 50 mg of alcohol in 100ml of blood (BAC: 0.05%)

(Note from your lecturer: No matter how powerful you felt after mastering Chemical Kinetics, **never rely on calculations to determine if you are safe to drive!)*

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Note: The current drink drive limit in Scotland is 50 mg of alcohol in 100ml of blood (BAC: 0.05%)

⚠

$$t_{1/2} = \frac{\ln 2}{k}$$

First, we calculate *k*:

$$4.5 \text{ h} = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{4.5h} = 0.154 \text{ h}^{-1}$$

And with *k*, we can calculate the time Jamie can go back home:

⚠

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

$$t_{\mathrm{JCGH}} = \frac{\ln \frac{[\mathrm{A}]_0}{\mathrm{A}}}{k} = \frac{\ln \frac{0.16}{0.05}}{0.154 \text{ h}^{-1}} = \frac{\ln 3.2}{0.154 \text{ h}^{-1}} = 7.55 \text{ hours after 10 PM}$$

$$t_{\mathrm{JCGH}} = \frac{\ln \frac{[\mathrm{A}]_0}{\mathrm{A}}}{k} = \frac{\ln \frac{0.16}{0.05}}{0.154\ \mathrm{h}^{-1}} = \frac{\ln 3.2}{0.154\ \mathrm{h}^{-1}} = 7.55 \text{ hours after 10 PM}$$

(5:33 AM Sunday)

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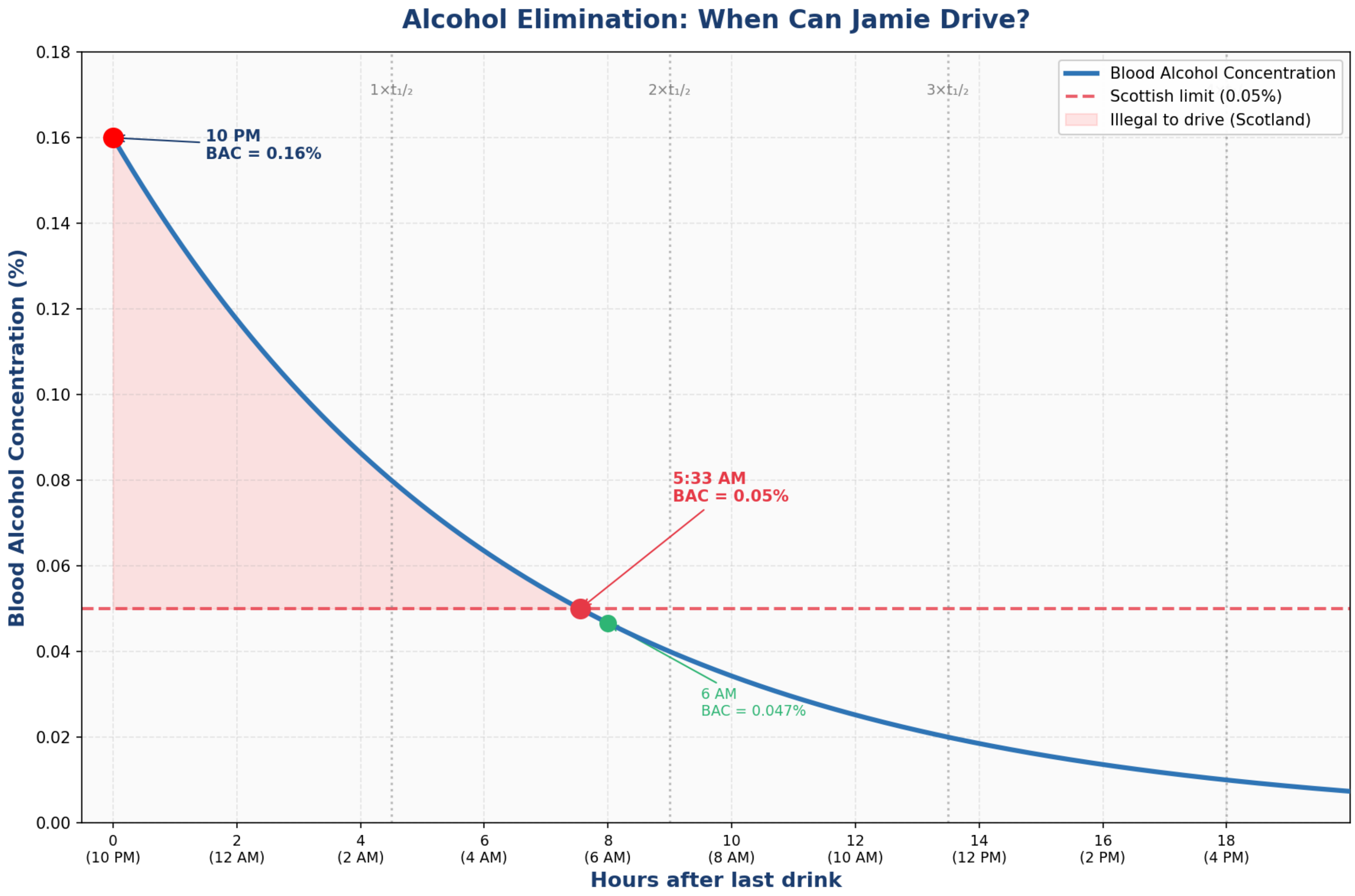
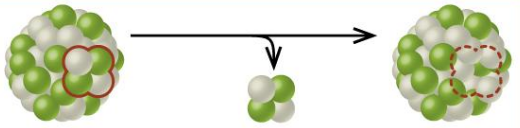
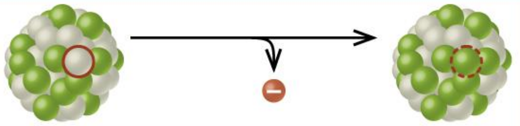
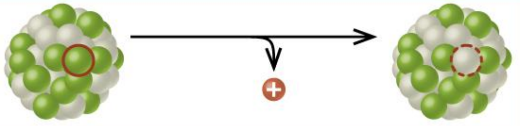


Nuclear chemistry

An atomic nucleus is stable when the strong nuclear force, which binds protons and neutrons together, is strong enough to overcome the electrostatic repulsion between the positively charged protons. (The role of the neutrons is to dilute the protons!: They contribute to the attractive strong force without adding electric repulsion)

When they are not stable, they decay following these first-order nuclear reactions:

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \quad {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \quad {}^{0}_{-1}e + {}_{Z+1}^{A}Y$		A: unchanged Z: increase by 1
Positron emission	${}^{A}_{Z}X \quad {}^{0}_{+1}e + {}_{Y-1}^{A}Y$		A: unchanged Z: decrease by 1

These decays are usually described with the half-lives of the isotopes

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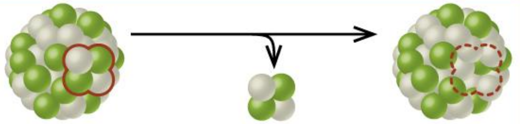
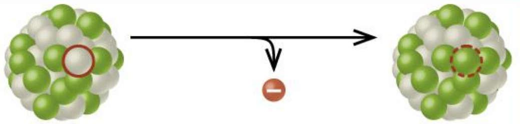
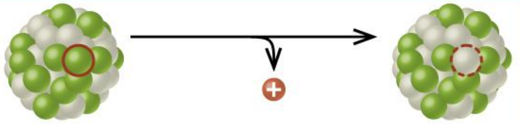
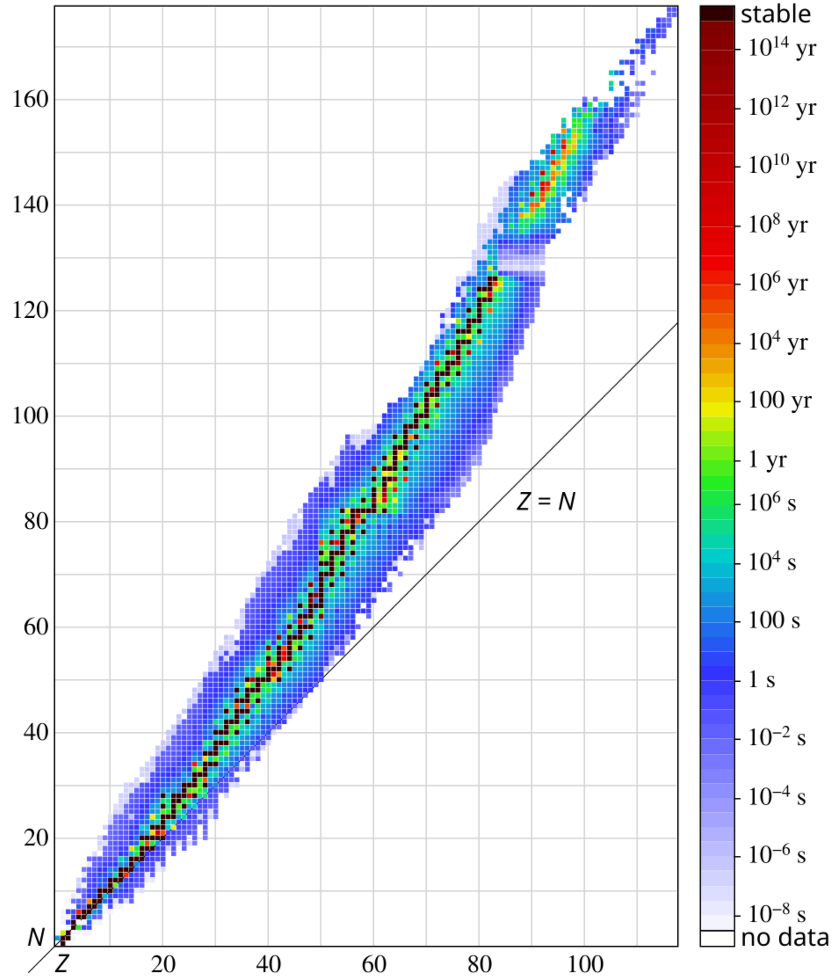
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}X \quad ^{4}_{2}He + ^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}X \quad ^{0}_{-1}e + ^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Positron emission	$^{A}_{Z}X \quad ^{0}_{+1}e + ^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

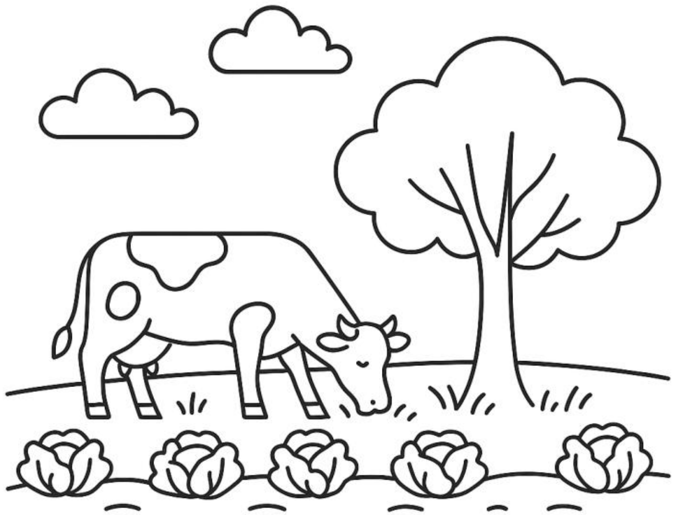
These decays, that are independent of temperature, pressure, or chemical environment, are usually described with the half-lives of the isotopes

Isotope half-lives



Carbon-14 dating

Fortunately, there is a radioactive isotope of carbon, carbon-14 (^{14}C), which decays with a half-life of about 5,730 years. It is continuously formed in the atmosphere and becomes incorporated into living organisms through processes such as photosynthesis and the food chain.



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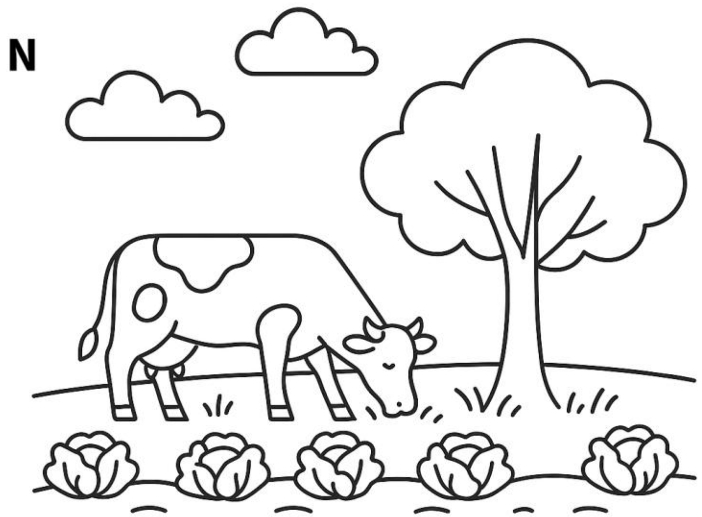

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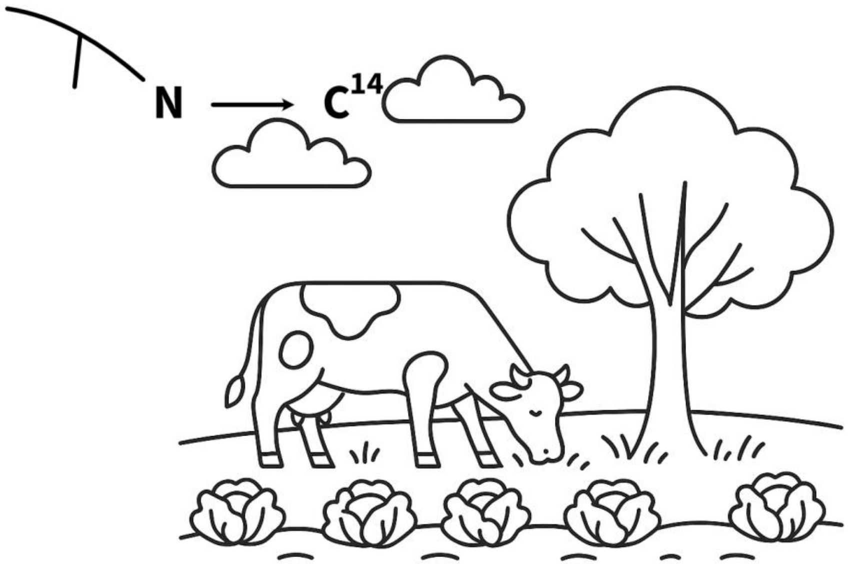

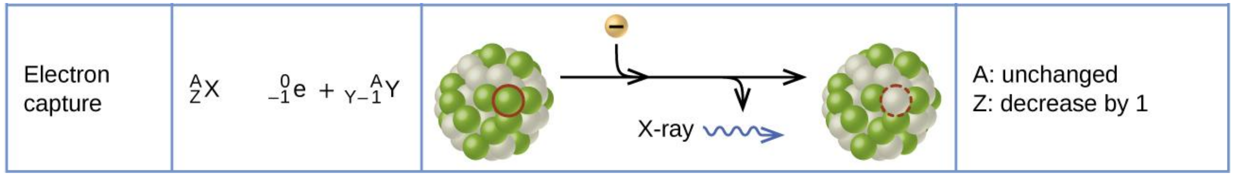

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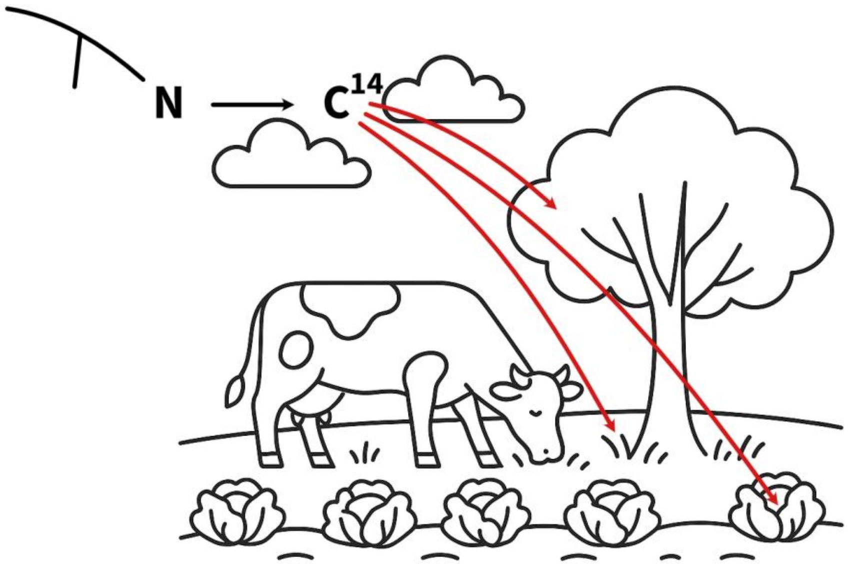

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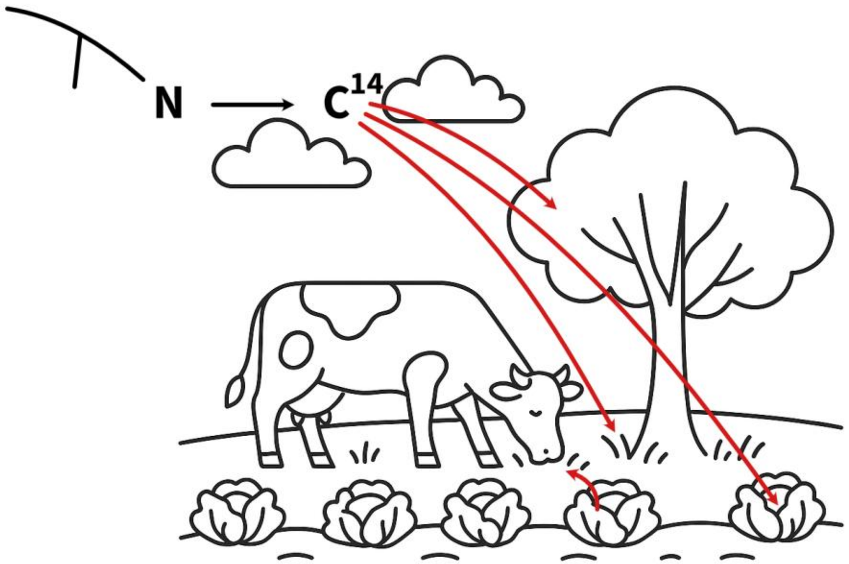

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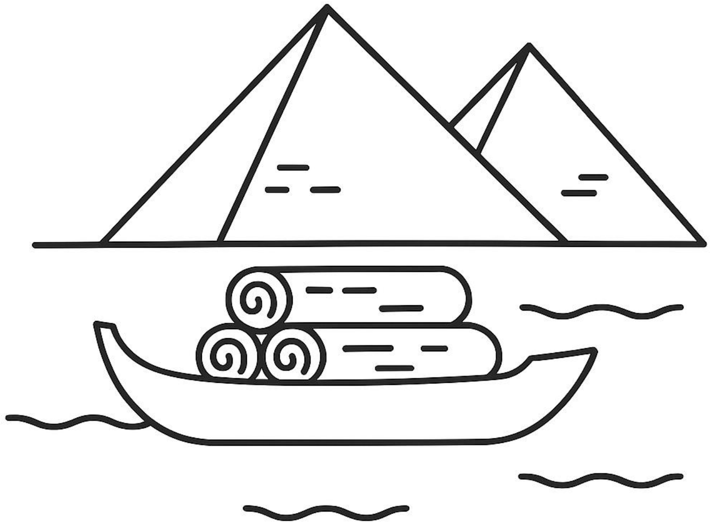
While an organism is alive, it constantly exchanges carbon with its environment, maintaining a roughly constant amount of carbon-14. However, once it dies, this exchange stops. From that moment on, the carbon-14 it contains begins to decay at a predictable rate.

$$^{14}C \rightarrow {}^{14}N + \beta^{-}$$



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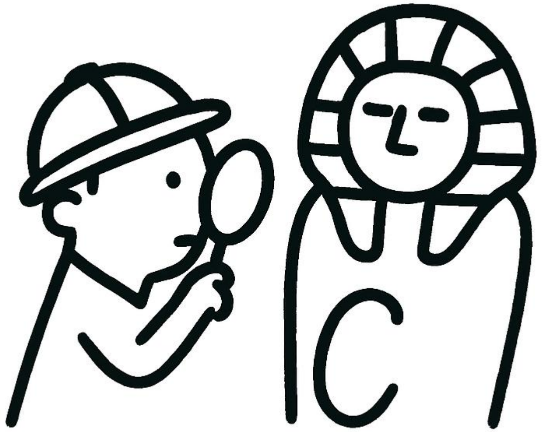
By measuring how much carbon-14 remains in an organic sample, we can determine how long it has been since the organism died. Now you know why carbon-14 dating is one of the most important and widely used tools in archaeology.



Exercise: the mistery of Rapa Nui

Rapa Nui (Easter Island) is one of the most remote inhabited places on Earth, located 3,700 km from South America and over 2,000 km from the nearest inhabited island. The island is famous for its nearly 1,000 monumental stone statues called moai, carved by the Polynesian settlers who arrived around 1200.

For decades, the popular narrative (made famous by Jared Diamond's book "Collapse") suggested that the Rapa Nui civilisation experienced a catastrophic collapse around 1600 CE due to deforestation and resource depletion, before the first arrival of Europeans, in 1722. Your mission is to prove or disprove this theory.
In order to do that, you joined an archaeological team excavating at Ahu Nau Nau (a ceremonial platform on Rapa Nui) and collected several samples for carbon-14 dating. These are the results:

Sample	Description	% ^{14}C remaining	Context
A	Charcoal from earliest settlement layer	90.5%	First colonisation
B	Wood fragment from moai transport ramp	93.2%	Statue building
C	Bone fragment from burial under ahu	95.8%	Late ceremonial use
D	Seed from red pigment pit	94.5%	Pigment production

What happened to the Rapa Nui civilisation?

Exercise: the mistery of Rapa Nui

First, we calculate the carbon-14 decay reaction constant:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5730\ \text{yr}} = 1.21 \times 10^{-4}\ \text{yr}^{-1}$$

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And then, we calculate the age of the samples

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

$$\Rightarrow \quad \ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \quad \Rightarrow \quad t_{\mathrm{samples}} = \frac{\ln \frac{[\mathrm{A}]_0}{\mathrm{A}}}{k} = \frac{\ln(\%\ ^{14}\mathrm{C\ remaining})}{k}$$

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$$t_A = \frac{\ln(100/90.5)}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = \frac{0.0998}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = 825\ \text{yr}$$

$$t_B = \frac{\ln(100/93.2)}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = \frac{0.0704}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = 582\ \text{yr}$$

$$t_C = \frac{\ln(100/95.8)}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = \frac{0.0431}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = 354\ \text{yr}$$

$$t_D = \frac{\ln(100/94.5)}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = \frac{0.0564}{1.21 \times 10^{-4}\ \text{yr}^{-1}} = 467\ \text{yr}$$

Exercise: the mistery of Rapa Nui

Sample	Description	% ^{14}C remaining	Context	Age	Year	Interpretation
A	Charcoal from earliest settlement layer	90.5%	First colonisation	825 yr	**~1201**	First settlement
B	Wood fragment from moai transport ramp	93.2%	Statue building	582 yr	**~1444**	Peak moai building
C	Bone fragment from burial under ahu	95.8%	Late ceremonial use	354 yr	**~1672**	After "collapse"
D	Seed from red pigment pit	94.5%	Pigment production	467 yr	**~1559**	Pigment production

Sample A dates to ~1201, consistent with current archaeological consensus that Polynesian colonisation occurred around 1200. Sample C dates to ~1672, showing that ceremonial activities continued 70 years after the supposed collapse. The dates show continuous cultural activity from settlement (~1201) through European contact (1722). There is no evidence of a sudden collapse in the archaeological record.

Reaction mechanisms

So far, we have obtained all our information about the reaction from experiments. From these measurements, we can determine the reaction orders and the rate constant. However, this approach does not tell us the individual molecular steps the reaction actually follows. These fundamental steps, which describe what is happening at the molecular level, are known as the reaction mechanism. A mechanism is proposed based on theoretical reasoning (as a hypothesis) and must then be tested and validated through lots of experiments.

Overall reaction

$$2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g)$$

Elementary Steps

1. $NO_2 + F_2 \rightarrow NO_2F + F$
2. $NO_2 + F \rightarrow NO_2F$

📖 Reaction mechanism: The sequence of elementary steps that connect reactants and products.
Reaction intermediates: Molecules or chemical species that form temporarily during the reaction and disappear before the final products are formed.

Elementary reactions

Molecularity	Elementary Reaction	Rate law
Unimolecular	A → products	$r = k\,[A]$
Bimolecular	A + A → products	$r = k\,[A]^2$
Bimolecular	A + B → products	$r = k\,[A][B]$
Termolecular	A + A + A →products	$r = k\,[A]^3$
Termolecular	A + A + B → products	$r = k\,[A]^2[B]$
Termolecular	A + B + C → products	$r = k\,[A][B][C]$

If a reaction is elementary, its rate law is based directly on its molecularity

Molecularity: The number of molecules that participate as reactants in an elementary reaction
Elementary reaction: Reactions that occur in a single event or step

Reaction mechanisms

Overall reaction

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

Elementary Steps

1. $NO_2 + F_2 \rightarrow NO_2F + F$ *Bimolecular: two molecules collide*
2. $NO_2 + F \rightarrow NO_2F$ *Bimolecular: uses the F atom produced in step 1*

Rate-determining step

Overall reaction

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

Elementary Steps

Slow	1. $NO_2 + F_2 \rightarrow NO_2F + F$	*Bimolecular: two molecules collide*
Fast	2. $NO_2 + F \rightarrow NO_2F$	*Bimolecular: uses the F atom produced in step 1*

The rate-determining step (RDS) is the slowest step in a reaction mechanism. It acts as a "bottleneck" that limits the overall reaction rate.

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$$r = k[NO_2][F_2]$$

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The rate-determining step (RDS) is the slowest step in a reaction mechanism. It acts as a "bottleneck" that limits the overall reaction rate.

$$r = k[NO_2][F_2]$$

This is our proposed reaction mechanism. If we carry out the experiment and find that the reaction is first order with respect to NO_2 and first order with respect to F_2, then all we can conclude is that the rate law predicted by the mechanism is consistent with the experimental results.

Challenge question

The decomposition of ozone in the atmosphere occurs according to the following overall reaction:

$$2\ O_3 \rightarrow 3\ O_2$$

Scientists have proposed the following two-step mechanism:

Step 1: $O_3 \rightarrow O_2 + O$ (fast, equilibrium)
Step 2: $O_3 + O \rightarrow 2\ O_2$ slow

a) Identify the intermediate in this mechanism
b) Which step is the rate-determining step?
c) What is the molecularity of each step?