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

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

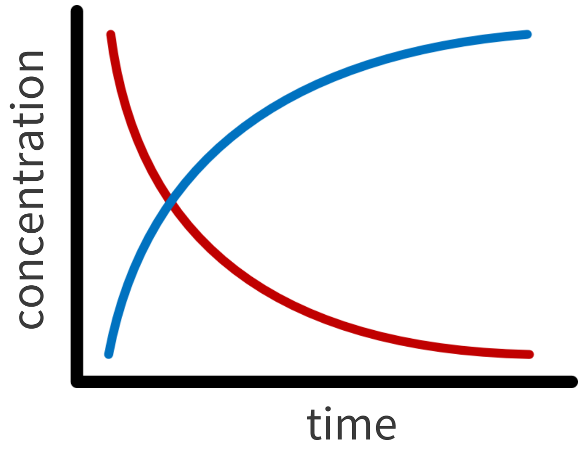
$$r = \frac{1}{\xi_P}\frac{\Delta[\text{Product}]}{\Delta t} = -\frac{1}{\xi_R}\frac{\Delta[\text{Reactant}]}{\Delta t}$$

Beer law

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

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

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

Order 3

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

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:

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

Therefore…

Exercise

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

Order 0

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

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

Order 1

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

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

Order 2

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

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

Order 3

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

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

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

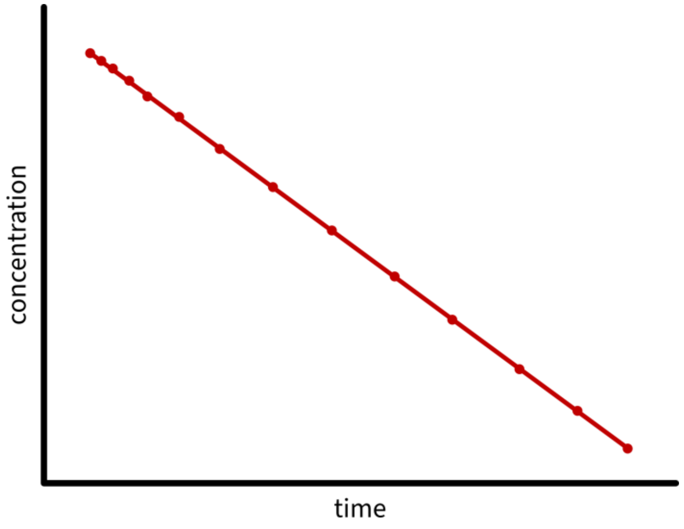
$$[\mathrm{A}] = [\mathrm{A}]_0 - kt$$

First-order

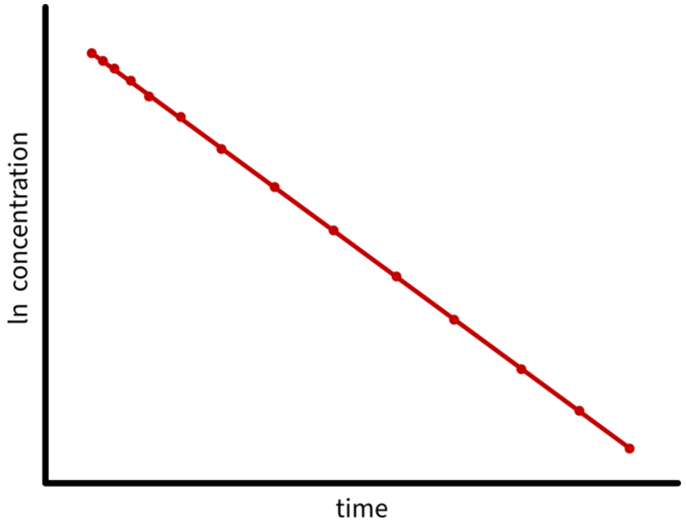
$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{-kt}$$

Second-order

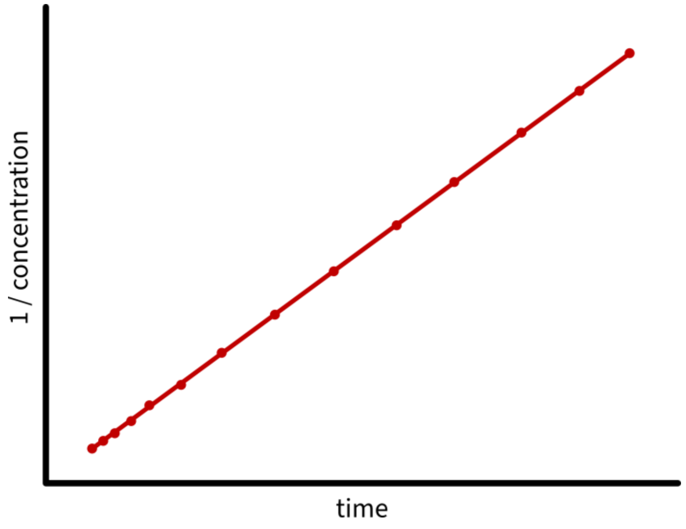
$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$



[A] vs t



ln [A] vs t



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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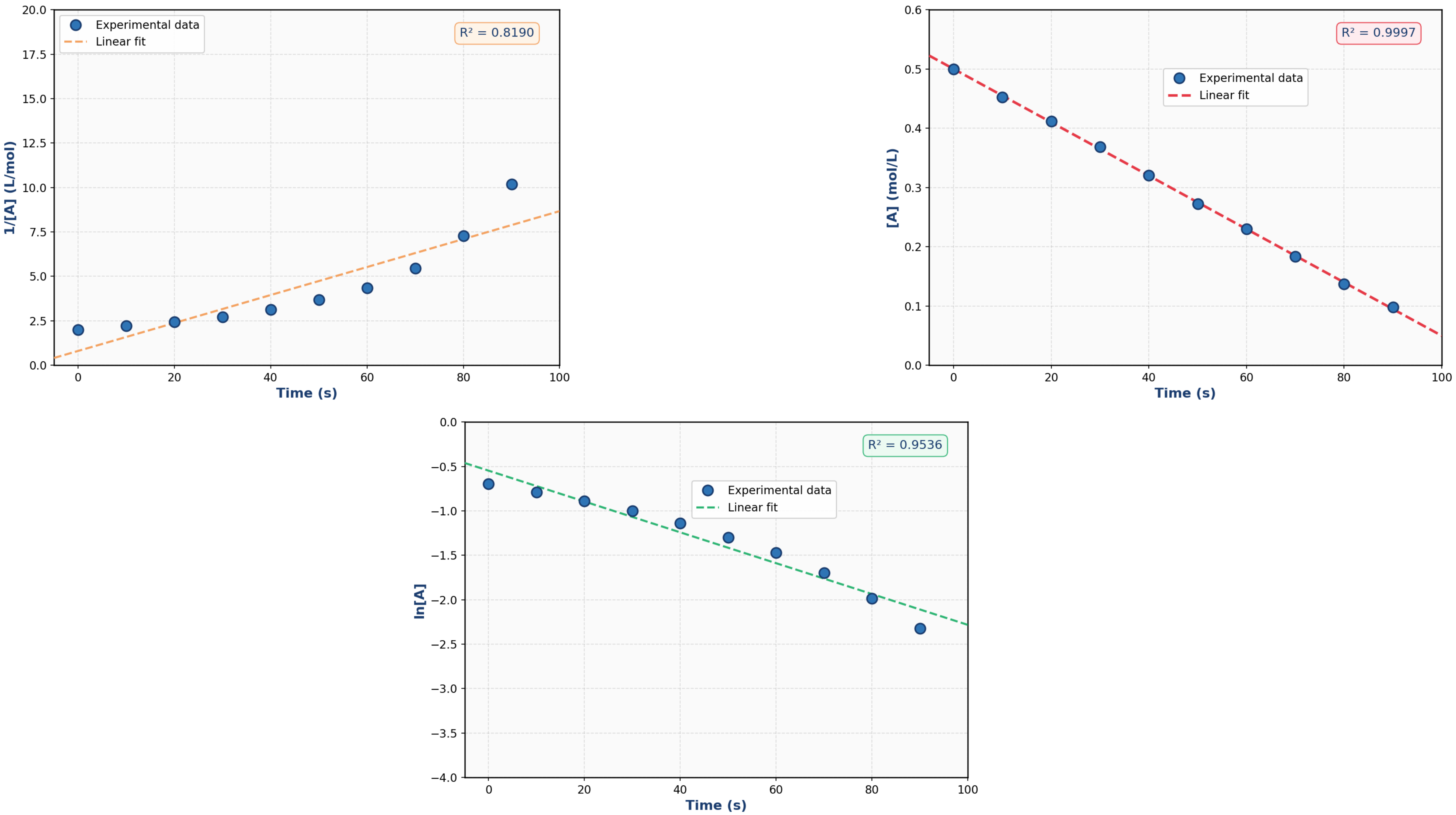
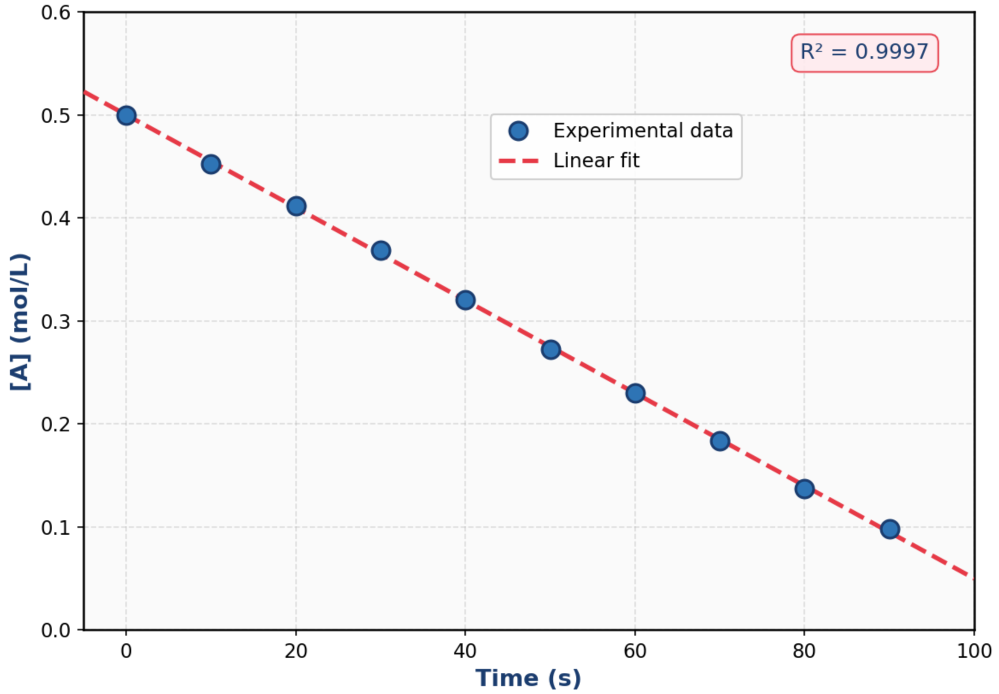
The concentration of ammonia was measured over time:

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

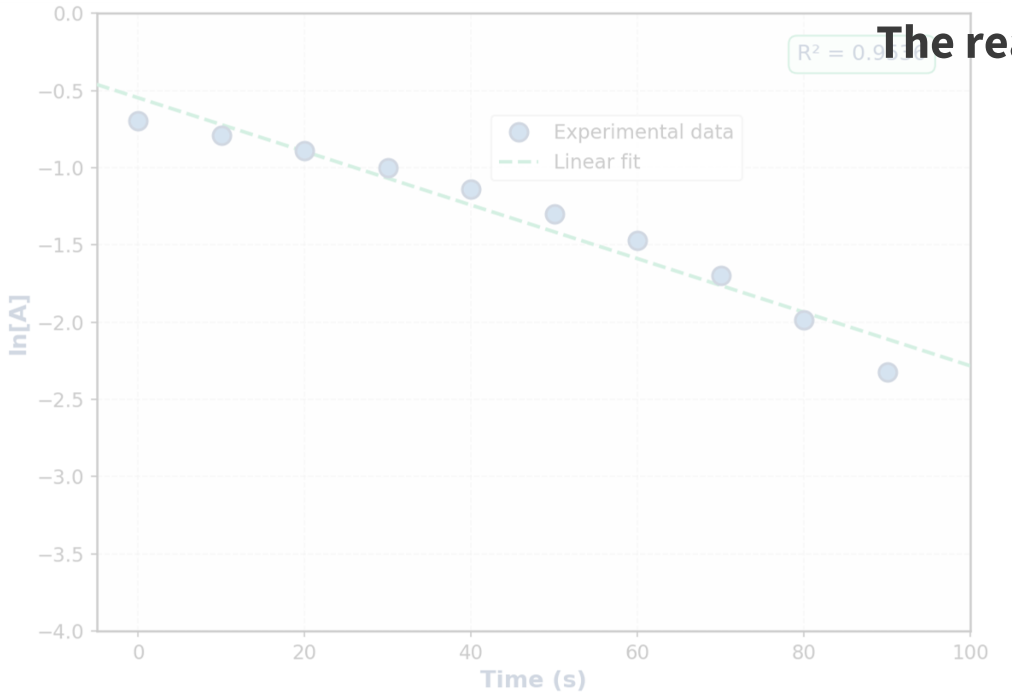
Determine the reaction order



Experimental data
Linear fit
R² = 0.8190
1/[A] (L/mol)
Time (s)
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
0
20
40
60
80
100
Experimental data
Linear fit
R² = 0.9997
[A] (mol/L)
Time (s)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Experimental data
Linear fit
R² = 0.9536
ln[A]
Time (s)
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
−3.5
−4.0

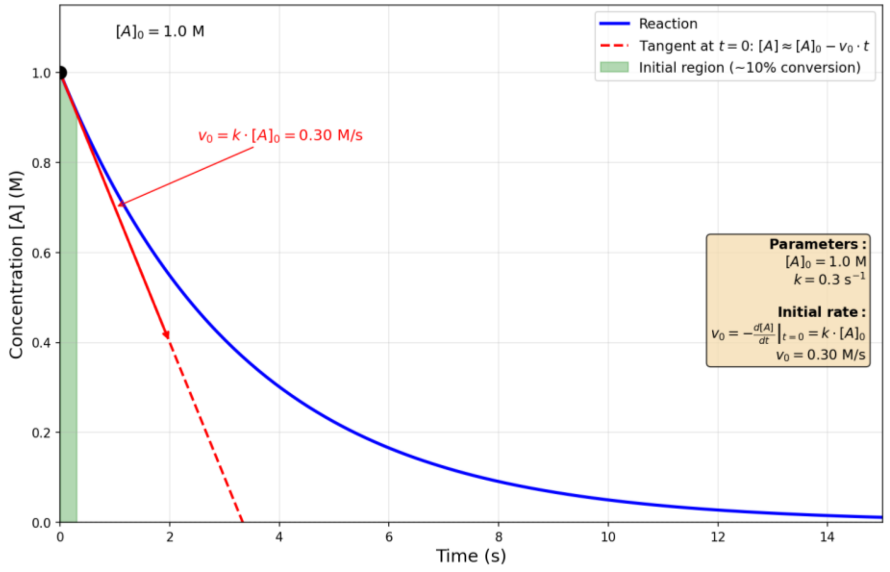


The reaction is zero-order with respect to A



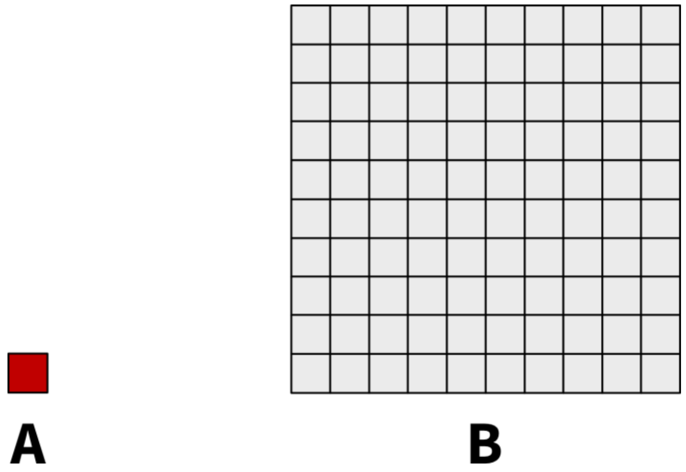
Previously on Chemical Kinetics...

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.

$$r = k'[\mathrm{O}] \qquad \text{where:} \quad k' = k[\mathrm{O_3}]$$

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

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

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

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

$$k = \frac{k'}{[\mathrm{O_3}]} \qquad k = \frac{2.4 \times 10^{6}\ \mathrm{s^{-1}}}{5.0 \times 10^{-4}\ \mathrm{M}} = 4.8 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$$

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:

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

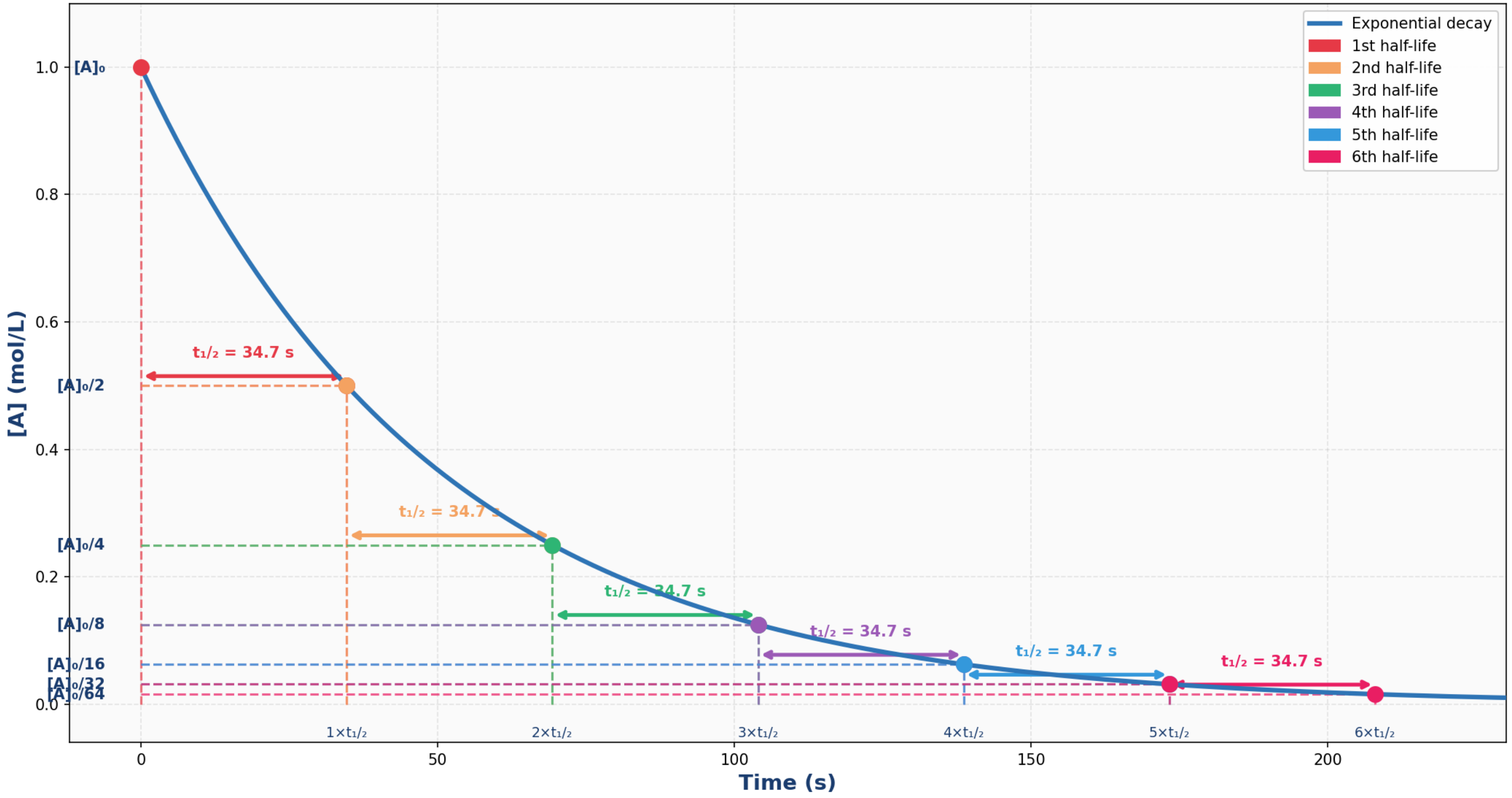
This is very interesting: This implies that the greater the amount of reactant present, the faster the reaction proceeds, but always in direct proportion. It does not matter how the system started or what happened before: the future behaviour depends only on its current value. That's why is the favourite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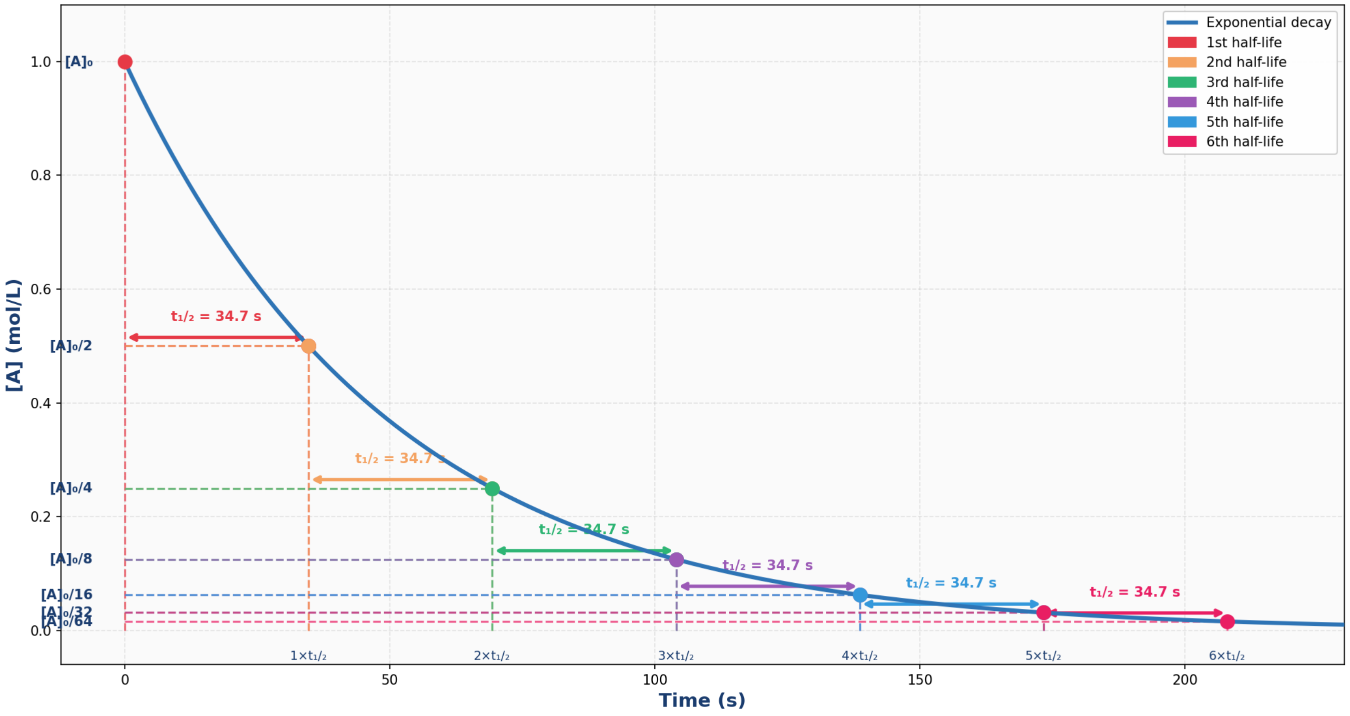

And it's super simple to calculate. You just need to check how long it takes for the reaction to reach half of its initial concentration:

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

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

(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.

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:

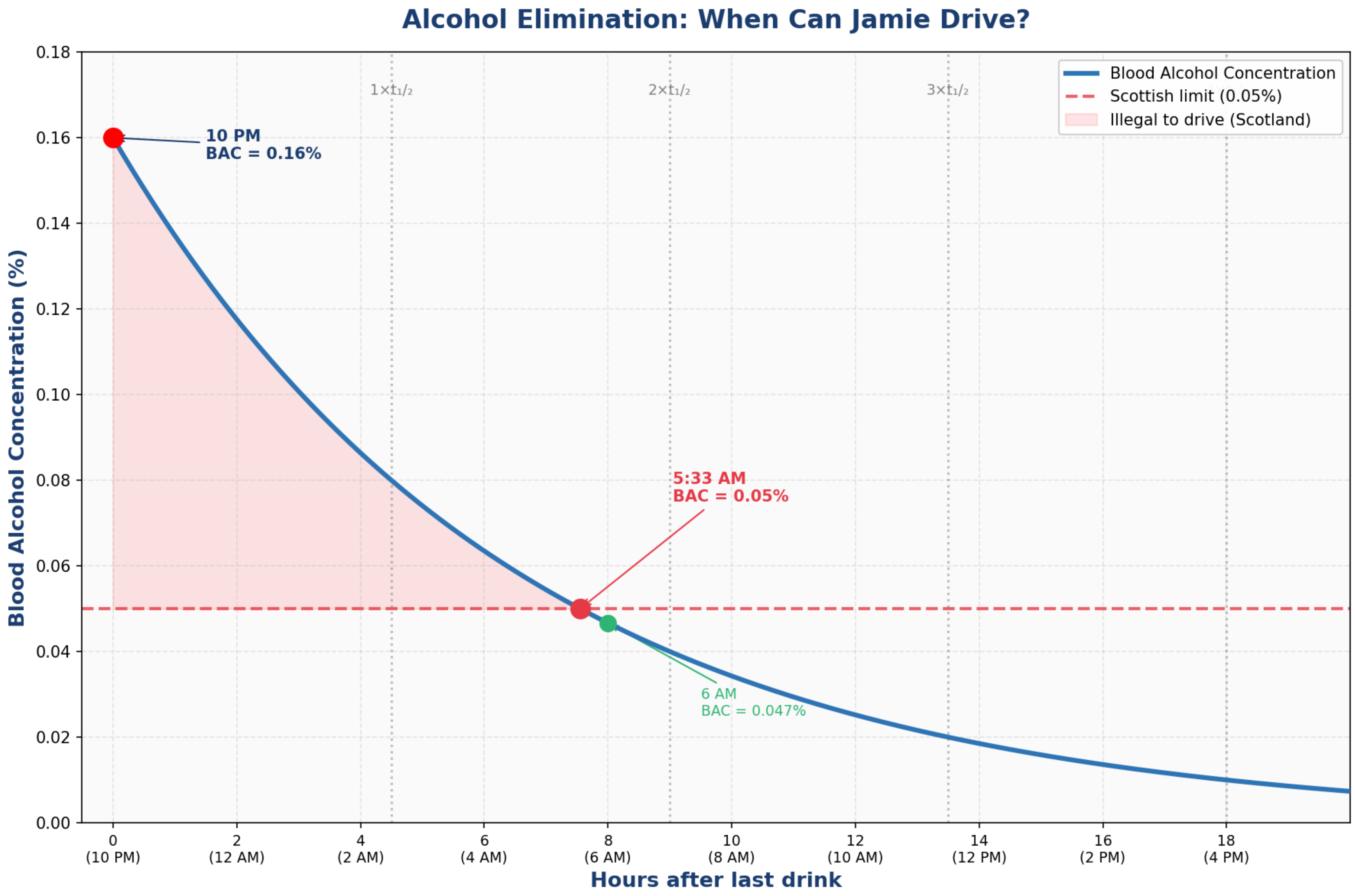
⚠

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

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

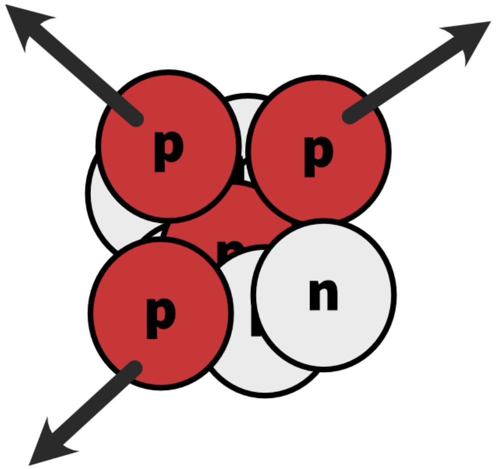
$$t_{\mathrm{JCGH}} = \frac{\ln \frac{[\mathrm{A}]_0}{\mathrm{A}}}{k} = \frac{\ln \frac{0.16}{0.05}}{0.154\ \mathrm{h}^{-1}} = \frac{\ln 3.2}{0.154\ \mathrm{h}^{-1}} = 7.55 \text{ hours after 10 PM}$$

(5:33 AM Sunday)

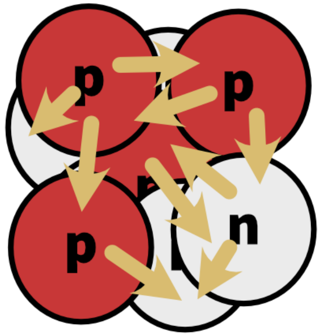


Nuclear chemistry

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)



Electric repulsion of protons strains the nucleus



but the strong nuclear force holds the nucleus together

Nuclear chemistry

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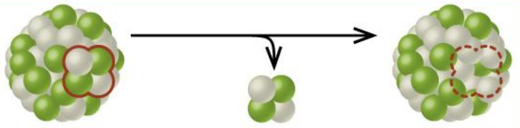
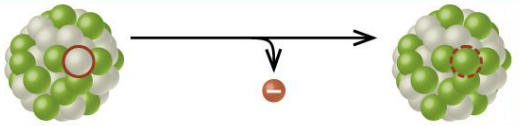
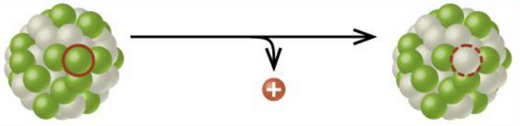
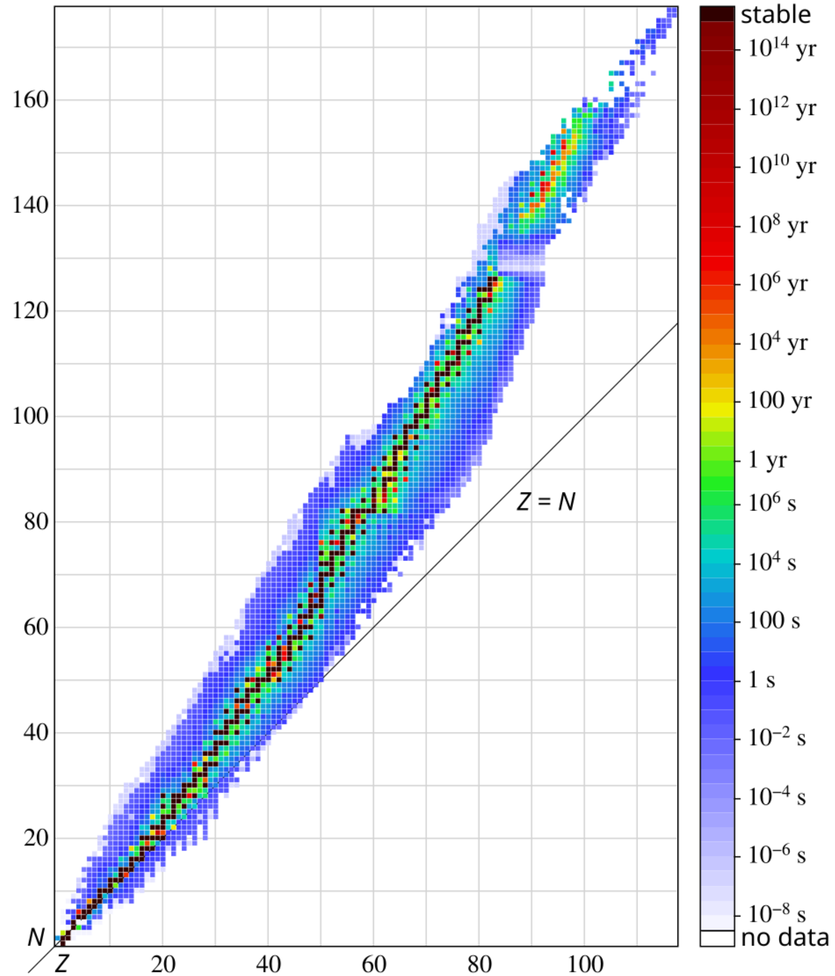
When they are not stable, they decay following these first-order nuclear reactions:

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	${}^{A}_{Z}X \quad {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		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

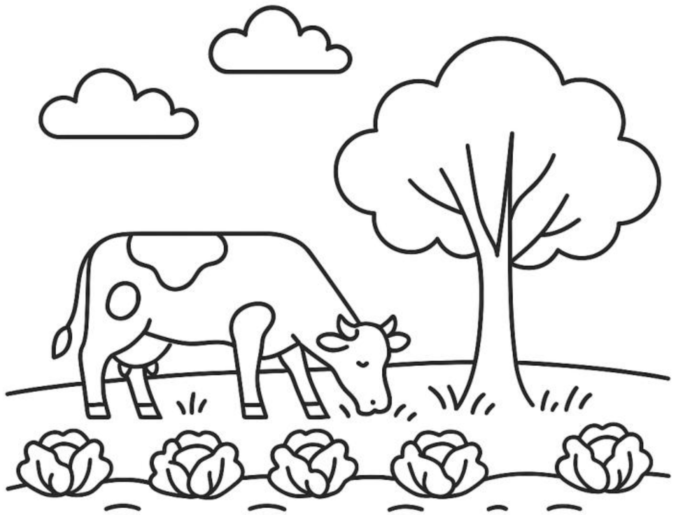
These decays, that are independent of temperature, pressure, or chemical environment, are usually described with the half-lives of the isotopes

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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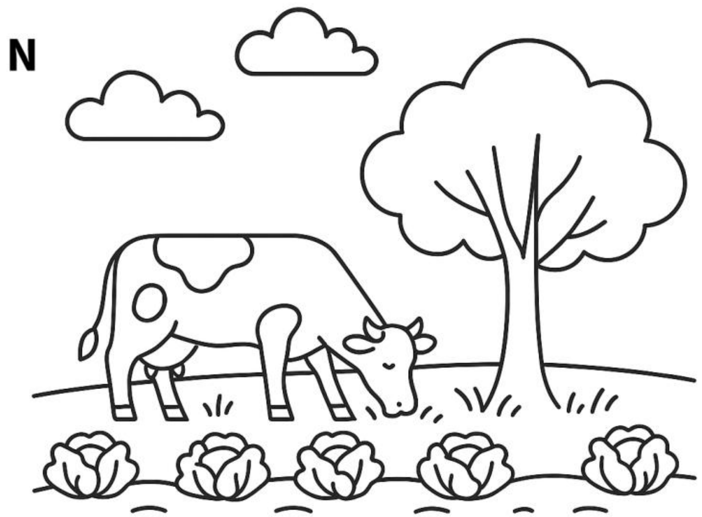

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🍎 **Resource in moodle:** Detection of cosmic particles with a fish tank

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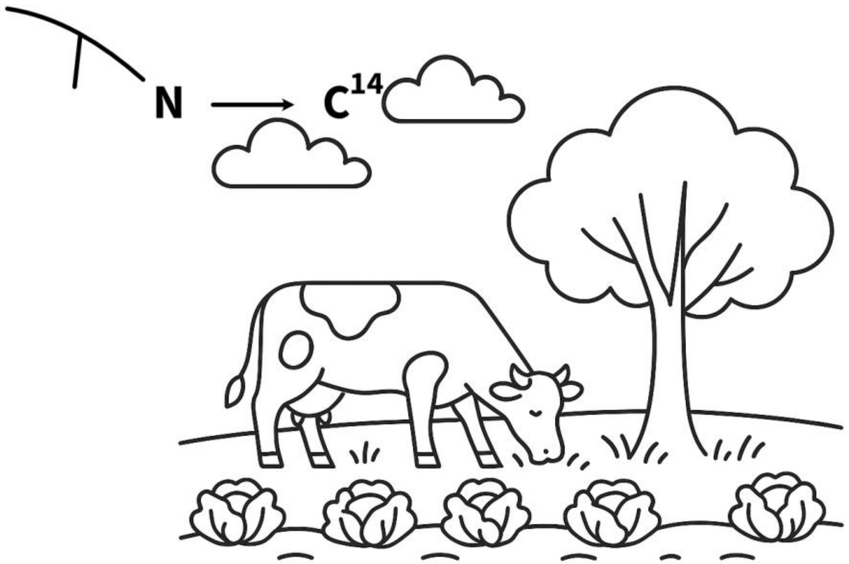

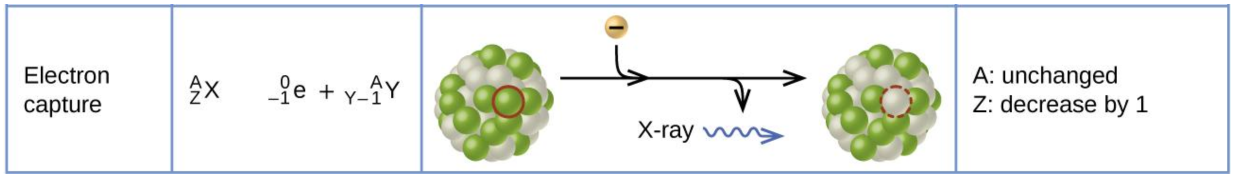

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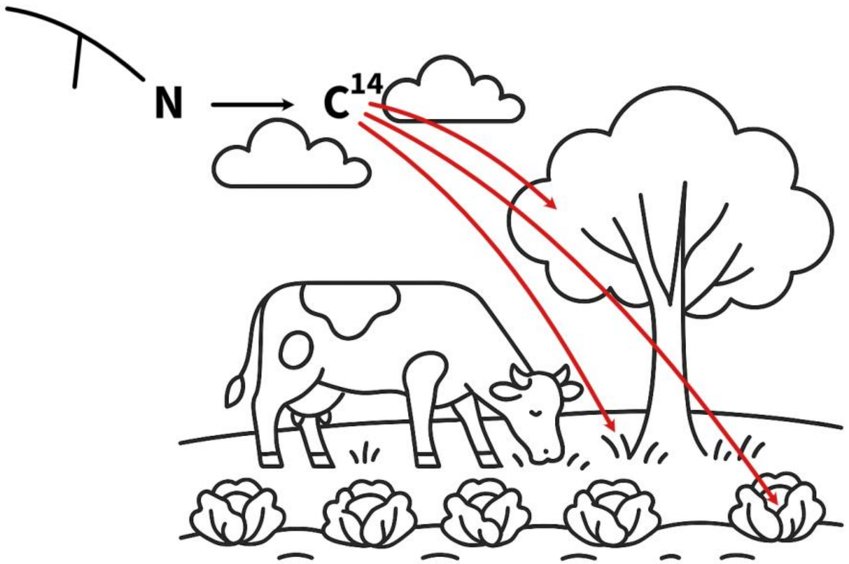

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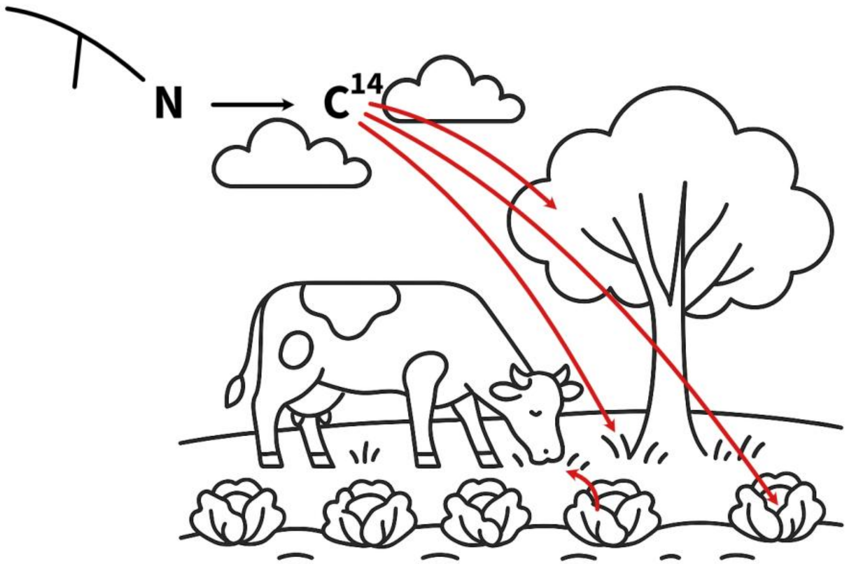

🍎 **Resource in moodle:** Detection of cosmic particles with a fish tank

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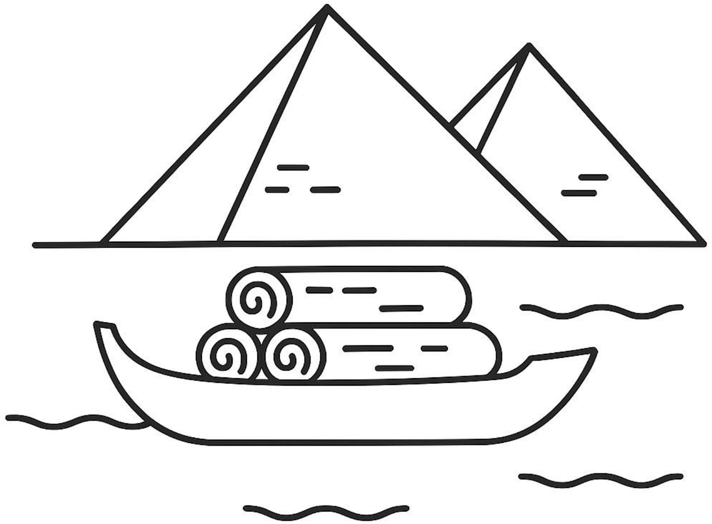
While an organism is alive, it constantly exchanges carbon with its environment, maintaining a roughly constant amount of carbon-14. However, once it dies, this exchange stops. From that moment on, the carbon-14 it contains begins to decay at a predictable rate.

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



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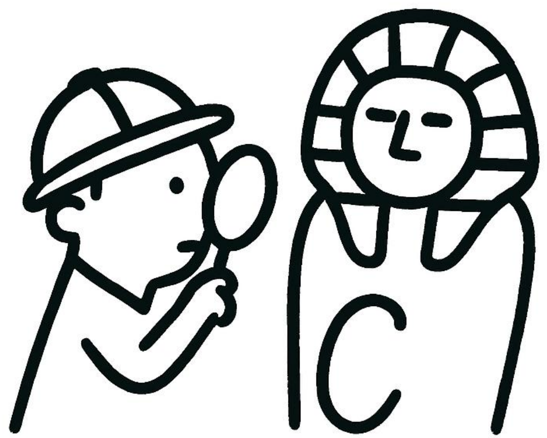
By measuring how much carbon-14 remains in an organic sample, we can determine how long it has been since the organism died. Now you know why carbon-14 dating is one of the most important and widely used tools in archaeology.



Challenge question: 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?