Science Fundamentals 1Y

Chemical Kinetics Workshop (Solutions)

Mario González-Jiménez
mario.gonzalezjimenez@glasgow.ac.uk

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Exercise 1: Determining Reaction Stoichiometry from Reaction Rates

Given information:

Species	Rate of change ($\mathrm{mol\,L^{-1}\,s^{-1}}$)
A	$-3.0 \cdot 10^{-3}$
B	$-1.5 \cdot 10^{-3}$
C	$+6.0 \cdot 10^{-3}$
D	$+1.5 \cdot 10^{-3}$

(a) Identify which species are reactants and which are products.
The sign of the rate of change tells us whether a species is being consumed or produced:

- A **negative** rate of change means the concentration is **decreasing** → the species is being **consumed** → it is a **reactant**
- A **positive** rate of change means the concentration is **increasing** → the species is being **produced** → it is a **product**

Looking at our data:

- A: rate = $-3.0 \cdot 10^{-3}\ \mathrm{mol\,L^{-1}\,s^{-1}}$ (negative) → **Reactant**
- B: rate = $-1.5 \cdot 10^{-3}\ \mathrm{mol\,L^{-1}\,s^{-1}}$ (negative) → **Reactant**
- C: rate = $+6.0 \cdot 10^{-3}\ \mathrm{mol\,L^{-1}\,s^{-1}}$ (positive) → **Product**
- D: rate = $+1.5 \cdot 10^{-3}\ \mathrm{mol\,L^{-1}\,s^{-1}}$ (positive) → **Product**

$$\boxed{\text{Reactants: A and B;}\quad \text{Products: C and D}}$$

(b) Determine the stoichiometric coefficients of the balanced equation.
For a general reaction:

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

The rates are related by:

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt}$$

This means that when we divide each rate by its stoichiometric coefficient, we get the same value (the overall reaction rate).

Step 1: Take the absolute values of all rates:

$$\begin{aligned}
|\text{Rate of A}| &= 3.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \\
|\text{Rate of B}| &= 1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \\
|\text{Rate of C}| &= 6.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \\
|\text{Rate of D}| &= 1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}
\end{aligned}$$

Step 2: Find the ratios by dividing all rates by the smallest rate:
The smallest rate is $1.5 \cdot 10^{-3}$ mol L^{-1} s^{-1}.

$$\begin{aligned}
\text{Ratio for A} &= \frac{3.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}} = 2 \\
\text{Ratio for B} &= \frac{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}} = 1 \\
\text{Ratio for C} &= \frac{6.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}} = 4 \\
\text{Ratio for D} &= \frac{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{1.5 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}} = 1
\end{aligned}$$

Step 3: These ratios give us the stoichiometric coefficients:

$$\boxed{a = 2, \quad b = 1, \quad c = 4, \quad d = 1}$$

(c) Write the balanced chemical equation.

Substituting the coefficients into the general equation:

$$\boxed{2\,\text{A} + \text{B} \longrightarrow 4\,\text{C} + \text{D}}$$

(d) Calculate the overall reaction rate.

The overall reaction rate is defined as the rate of change of any species divided by its stoichiometric coefficient (with the appropriate sign).

Using species A:

$$r = -\frac{1}{a}\frac{d[\text{A}]}{dt}$$

We have $a = 2$ and $\frac{d[\text{A}]}{dt} = -3.0 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Substituting:

$$r = -\frac{1}{2} \times (-3.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1})$$

Multiplying the negative signs:

$$r = \frac{1}{2} \times 3.0 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$r = \boxed{1.5 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$$

Exercise 2: The Beer–Lambert Law

Given information:

- Molar absorption coefficient: $\varepsilon = 1.25 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$
- Path length: $l = 1.00\,\mathrm{cm}$

The Beer–Lambert law is:

$$A = \varepsilon \cdot l \cdot c$$

(a) A freshly prepared solution of X shows an absorbance of $A = 0.875$. Calculate the initial concentration of X.

Step 1: Rearrange the Beer–Lambert law to solve for concentration c:

$$A = \varepsilon \cdot l \cdot c$$

Dividing both sides by $\varepsilon \cdot l$:

$$c = \frac{A}{\varepsilon \cdot l}$$

Step 2: Substitute the known values:

$$c = \frac{0.875}{(1.25 \cdot 10^4\ \mathrm{L\,mol^{-1}\,cm^{-1}}) \times (1.00\ \mathrm{cm})}$$

Step 3: Perform the division:

$$c = \frac{0.875}{1.25 \cdot 10^4\ \mathrm{L\ mol^{-1}}}$$

$$\boxed{c = 7.00 \cdot 10^{-5}\ \mathrm{mol\,L^{-1}}}$$

(b) After $10\,\mathrm{min}$, the absorbance has decreased to $A = 0.625$. What is the concentration of X at this time?

Step 1: Use the same rearranged equation:

$$c = \frac{A}{\varepsilon \cdot l}$$

Step 2: Substitute the new absorbance value:

$$c = \frac{0.625}{(1.25 \cdot 10^4\ \mathrm{L\,mol^{-1}\,cm^{-1}}) \times (1.00\ \mathrm{cm})}$$

Step 3: Perform the division:

$$c = \frac{0.625}{1.25 \cdot 10^4\ \mathrm{L\ mol^{-1}}}$$

$$\boxed{c = 5.00 \cdot 10^{-5}\ \mathrm{mol\,L^{-1}}}$$

Exercise 3: Calculating Average Reaction Rates

Given information:

Time (s)	[A] ($\mathrm{mol\,L^{-1}}$)
0	0.500
20	0.389
40	0.303
60	0.236
80	0.184
100	0.143

We assume an stoichiometric coefficient of 1.
The formula for the average rate of disappearance is:

$$\text{Average rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{[\mathrm{A}]_{t_2} - [\mathrm{A}]_{t_1}}{t_2 - t_1}$$

(a) Calculate the average rate of disappearance of A over the interval $t = 0\,\mathrm{s}$ to $t = 20\,\mathrm{s}$.

Step 1: Identify the concentrations at the two times:

$$[\mathrm{A}]_{t_1} = [\mathrm{A}]_0 = 0.500\ \mathrm{mol\,L^{-1}}$$
$$[\mathrm{A}]_{t_2} = [\mathrm{A}]_{20} = 0.389\ \mathrm{mol\,L^{-1}}$$

Step 2: Calculate $\Delta[\mathrm{A}]$:

$$\Delta[\mathrm{A}] = [\mathrm{A}]_{t_2} - [\mathrm{A}]_{t_1} = 0.389\ \mathrm{mol\,L^{-1}} - 0.500\ \mathrm{mol\,L^{-1}} = -0.111\ \mathrm{mol\,L^{-1}}$$

Step 3: Calculate Δt:

$$\Delta t = t_2 - t_1 = 20\ \mathrm{s} - 0\ \mathrm{s} = 20\ \mathrm{s}$$

Step 4: Calculate the average rate:

$$\text{Average rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{-0.111\ \mathrm{mol\,L^{-1}}}{20\ \mathrm{s}}$$

The two negative signs cancel:

$$\boxed{\text{Average rate} = 5.55 \cdot 10^{-3}\ \mathrm{mol\,L^{-1}\,s^{-1}}}$$

(b) Calculate the average rate over the interval $t = 80\,\mathrm{s}$ to $t = 100\,\mathrm{s}$.

Step 1: Identify the concentrations:

$$[\mathrm{A}]_{t_1} = [\mathrm{A}]_{80} = 0.184\ \mathrm{mol\,L^{-1}}$$
$$[\mathrm{A}]_{t_2} = [\mathrm{A}]_{100} = 0.143\ \mathrm{mol\,L^{-1}}$$

Step 2: Calculate $\Delta[\mathrm{A}]$:

$$\Delta[\mathrm{A}] = 0.143\ \mathrm{mol\,L^{-1}} - 0.184\ \mathrm{mol\,L^{-1}} = -0.041\ \mathrm{mol\,L^{-1}}$$

Step 3: Calculate Δt:

$$\Delta t = 100\ \mathrm{s} - 80\ \mathrm{s} = 20\ \mathrm{s}$$

Step 4: Calculate the average rate:

$$\text{Average rate} = -\frac{-0.041\ \text{mol}\,\text{L}^{-1}}{20\ \text{s}}$$

$$\boxed{\text{Average rate} = 2.05 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$$

(c) Compare your answers to (a) and (b). Explain why they differ.
Comparison:

- Rate at the beginning (0–20 s): $5.55 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$
- Rate near the end (80–100 s): $2.05 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$

Let's calculate the ratio:

$$\frac{\text{Rate at beginning}}{\text{Rate at end}} = \frac{5.55 \cdot 10^{-3}}{2.05 \cdot 10^{-3}} = \frac{5.55}{2.05} = 2.7$$

Explanation:
The rate at the beginning is approximately **2.7 times larger** than the rate near the end. This is because:

1. Reaction rates typically depend on reactant concentrations.
2. At the beginning ($t = 0$–20 s), [A] is high (around 0.5 M).
3. Near the end ($t = 80$–100 s), [A] is much lower (around 0.16 M).
4. As the reaction proceeds and [A] decreases, there are fewer reactant molecules available to react, so the rate decreases.

(d) Calculate the average rate over the entire experiment ($t = 0\,\text{s}$ to $t = 100\,\text{s}$).
Step 1: Identify the concentrations:

$$[\text{A}]_{t_1} = [\text{A}]_0 = 0.500\ \text{mol}\,\text{L}^{-1}$$
$$[\text{A}]_{t_2} = [\text{A}]_{100} = 0.143\ \text{mol}\,\text{L}^{-1}$$

Step 2: Calculate $\Delta[\text{A}]$:

$$\Delta[\text{A}] = 0.143\ \text{mol}\,\text{L}^{-1} - 0.500\ \text{mol}\,\text{L}^{-1} = -0.357\ \text{mol}\,\text{L}^{-1}$$

Step 3: Calculate Δt:

$$\Delta t = 100\ \text{s} - 0\ \text{s} = 100\ \text{s}$$

Step 4: Calculate the average rate:

$$\text{Average rate} = -\frac{-0.357\ \text{mol}\,\text{L}^{-1}}{100\ \text{s}}$$

$$\boxed{\text{Average rate} = 3.57 \cdot 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$$

Note: This value lies between the rates calculated in (a) and (b), as expected for an average over the entire time period.

(e) Why is the instantaneous rate generally more useful than the average rate in kinetic studies?

Instantaneous rate is the rate at a specific moment in time, corresponding to a particular set of concentrations. It is especially useful because it allows us to establish the mathematical relationship between rate and concentration (the rate law) and to determine reaction orders and rate constants.

Exercise 4: Identifying Reaction Orders from Rate Laws

Background: For a rate law of the form:

$$r = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^p \cdots$$

- The **order with respect to each reactant** is the exponent on that reactant's concentration.
- The **overall reaction order** is the sum of all the exponents.
- The **units of k** can be found by dimensional analysis.

Finding units of k:
The rate always has units of $\mathrm{mol\,L^{-1}\,s^{-1}}$. If the overall order is n:

$$\mathrm{mol\,L^{-1}\,s^{-1}} = [k] \times (\mathrm{mol\,L^{-1}})^n$$

Solving for $[k]$:

$$[k] = \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^n} = \mathrm{mol}^{1-n}\mathrm{L}^{n-1}\mathrm{s}^{-1}$$

Or equivalently:

$$[k] = \mathrm{L}^{n-1}\mathrm{mol}^{1-n}\mathrm{s}^{-1}$$

(a) $r = k[\mathrm{NO}]^2[\mathrm{O_2}]$
Step 1: Identify orders with respect to each reactant:

- Order in NO: the exponent is 2
- Order in O_2: the exponent is 1

Step 2: Calculate overall order:

$$\text{Overall order} = 2 + 1 = 3$$

Step 3: Determine units of k (for $n = 3$):

$$[k] = \mathrm{L}^{3-1}\mathrm{mol}^{1-3}\mathrm{s}^{-1} = \mathrm{L}^2\mathrm{mol}^{-2}\mathrm{s}^{-1}$$

$$\boxed{\text{Order in NO: 2;} \quad \text{Order in } \mathrm{O_2}\text{: 1;} \quad \text{Overall order: 3;} \quad \text{Units of } k: \mathrm{L^2mol^{-2}s^{-1}}}$$

(b) $r = k[\mathrm{H_2O_2}]$
Step 1: Identify order:

- Order in H_2O_2: the exponent is 1

Step 2: Overall order:

$$\text{Overall order} = 1$$

Step 3: Units of k (for $n = 1$):

$$[k] = \mathrm{L}^{1-1}\mathrm{mol}^{1-1}\mathrm{s}^{-1} = \mathrm{L}^0\mathrm{mol}^0\mathrm{s}^{-1} = \mathrm{s}^{-1}$$

$$\boxed{\text{Order in } \mathrm{H_2O_2}\text{: 1;} \quad \text{Overall order: 1;} \quad \text{Units of } k: \mathrm{s^{-1}}}$$

(c) $r = k[\mathrm{NO}]^2[\mathrm{Cl_2}]$
Step 1: Identify orders:

- Order in NO: 2
- Order in Cl_2: 1

Step 2: Overall order:

$$\text{Overall order} = 2 + 1 = 3$$

Step 3: Units of k (for $n = 3$):

$$[k] = \mathrm{L^2 mol^{-2} s^{-1}}$$

$$\boxed{\text{Order in NO: 2;}\quad \text{Order in Cl}_2\text{: 1;}\quad \text{Overall order: 3;}\quad \text{Units of } k : \mathrm{L^2 mol^{-2} s^{-1}}}$$

(d) $r = k$ (for the decomposition of NH_3 on a tungsten surface)
Step 1: Identify order:
The rate does not depend on any concentration. This is a **zero-order** reaction.
Step 2: Overall order:

$$\text{Overall order} = 0$$

Step 3: Units of k (for $n = 0$):

$$[k] = \mathrm{L^{0-1} mol^{1-0} s^{-1}} = \mathrm{L^{-1} mol^{1} s^{-1}} = \mathrm{mol\,L^{-1}\,s^{-1}}$$

$$\boxed{\text{Overall order: 0;}\quad \text{Units of } k : \mathrm{mol\,L^{-1}\,s^{-1}}}$$

Remember: Zero-order kinetics often occurs in surface-catalysed reactions when the surface is saturated with reactant.

Exercise 5: Determining Reaction Orders and Rate Constants

Reaction: $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$
Given data:

Experiment	[NO] ($\mathrm{mol\,L^{-1}}$)	[Cl_2] ($\mathrm{mol\,L^{-1}}$)	Initial rate ($\mathrm{mol\,L^{-1}\,s^{-1}}$)
1	0.010	0.010	$1.2 \cdot 10^{-4}$
2	0.010	0.020	$2.4 \cdot 10^{-4}$
3	0.020	0.020	$9.6 \cdot 10^{-4}$

The rate law has the form:

$$r = k[\mathrm{NO}]^m[\mathrm{Cl_2}]^n$$

(a) Determine the order of the reaction with respect to NO.
Strategy: Compare two experiments where [Cl_2] is constant but [NO] changes.
Experiments 2 and 3 both have [Cl_2] = 0.020 M.
Step 1: Write the rate expressions for experiments 2 and 3:

$$r_2 = k[\mathrm{NO}]_2^m[\mathrm{Cl_2}]_2^n = k(0.010\ \mathrm{mol\,L^{-1}})^m(0.020\ \mathrm{mol\,L^{-1}})^n$$
$$r_3 = k[\mathrm{NO}]_3^m[\mathrm{Cl_2}]_3^n = k(0.020\ \mathrm{mol\,L^{-1}})^m(0.020\ \mathrm{mol\,L^{-1}})^n$$

Step 2: Divide Rate$_3$ by Rate$_2$:

$$\frac{r_3}{r_2} = \frac{k(0.020\ \mathrm{mol\,L^{-1}})^m(0.020\ \mathrm{mol\,L^{-1}})^n}{k(0.010\ \mathrm{mol\,L^{-1}})^m(0.020\ \mathrm{mol\,L^{-1}})^n}$$

Step 3: Simplify (the k and $(0.020\ \mathrm{mol\,L^{-1}})^n$ terms cancel):

$$\frac{r_3}{r_2} = \frac{(0.020\ \mathrm{mol\,L^{-1}})^m}{(0.010\ \mathrm{mol\,L^{-1}})^m} = \left(\frac{0.020\ \mathrm{mol\,L^{-1}}}{0.010\ \mathrm{mol\,L^{-1}}}\right)^m = 2^m$$

Step 4: Calculate the left side using the experimental rates:

$$\frac{r_3}{r_2} = \frac{9.6 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{2.4 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}} = 4$$

Step 5: Solve for m:

$$2^m = 4$$

Since $2^2 = 4$:

$$\boxed{m = 2}$$

The reaction is **second order** with respect to NO.

(b) Determine the order of the reaction with respect to Cl$_2$.

Strategy: Compare two experiments where [NO] is constant but [Cl$_2$] changes. Experiments 1 and 2 both have [NO] = 0.010 M.

Step 1: Write the rate expressions:

$$r_1 = k(0.010\ \mathrm{mol\,L^{-1}})(0.010\ \mathrm{mol\,L^{-1}})^n$$
$$r_2 = k(0.010\ \mathrm{mol\,L^{-1}})(0.020\ \mathrm{mol\,L^{-1}})^n$$

Step 2: Divide Rate$_2$ by Rate$_1$:

$$\frac{r_2}{r_1} = \frac{k(0.010\ \mathrm{mol\,L^{-1}})(0.020\ \mathrm{mol\,L^{-1}})^n}{k(0.010\ \mathrm{mol\,L^{-1}})(0.010\ \mathrm{mol\,L^{-1}})^n} = \left(\frac{0.020\ \mathrm{mol\,L^{-1}}}{0.010\ \mathrm{mol\,L^{-1}}}\right)^n = 2^n$$

Step 3: Calculate the left side:

$$\frac{r_2}{r_1} = \frac{2.4 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{1.2 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}} = 2$$

Step 4: Solve for n:

$$2^n = 2$$

Since $2^1 = 2$:

$$\boxed{n = 1}$$

The reaction is **first order** with respect to Cl$_2$.

(c) Write the rate law for this reaction.

Substituting $m = 2$ and $n = 1$:

$$\boxed{r = k[\mathrm{NO}]^2[\mathrm{Cl_2}]}$$

The overall reaction order is $2 + 1 = 3$ (third order).

(d) Calculate the value of the rate constant k, including its units.

Step 1: Rearrange the rate law to solve for k:

$$k = \frac{r}{[\mathrm{NO}]^2[\mathrm{Cl_2}]}$$

Step 2: Use data from experiment 1:

$$k = \frac{1.2 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{(0.010\ \mathrm{mol\,L^{-1}})^2 \times (0.010\ \mathrm{mol\,L^{-1}})}$$

Step 2: Perform the division:

$$k = \frac{1.2 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{1.0 \cdot 10^{-6}\ \mathrm{mol^3L^{-3}}}$$

$$\boxed{k = 120\ \mathrm{mol^{-2}L^2s^{-1}}}$$

(e) Predict the initial rate when [NO] $= 0.015\,\mathrm{mol\,L^{-1}}$ and [Cl$_2$] $= 0.025\,\mathrm{mol\,L^{-1}}$.
Step 1: Write the rate law with the known value of k:

$$r = k[\mathrm{NO}]^2[\mathrm{Cl_2}] = 120[\mathrm{NO}]^2[\mathrm{Cl_2}]$$

Step 2: Substitute the given concentrations:

$$r = 120\ \mathrm{mol^{-2}L^2s^{-1}} \times (0.015\ \mathrm{mol\,L^{-1}})^2 \times (0.025\ \mathrm{mol\,L^{-1}})$$

Step 3: Multiply all terms:

$$r = 120\ \mathrm{mol^{-2}L^2s^{-1}} \times 2.25 \cdot 10^{-4}\ \mathrm{mol^2L^{-2}} \times 0.025\ \mathrm{mol\,L^{-1}}$$

$$r = 120\ \mathrm{mol^{-2}L^2s^{-1}} \times 5.625 \cdot 10^{-6}\ \mathrm{mol^3L^{-3}}$$

$$\boxed{r = 6.75 \cdot 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}$$

Exercise 6: Graphical Determination of Reaction Order

Reaction: $2\,\mathrm{NO_2(g)} \longrightarrow 2\,\mathrm{NO(g)} + \mathrm{O_2(g)}$

(a) Complete the table by calculating ln[NO$_2$] and 1/[NO$_2$] for each time point.
Here is the complete table:

Time (s)	[NO$_2$] (mol L^{-1})	ln[NO$_2$]	1/[NO$_2$] (L mol^{-1})
0	0.0100	−4.605	100
50	0.0079	−4.840	127
100	0.0065	−5.036	154
150	0.0055	−5.203	182
200	0.0048	−5.340	208
300	0.0038	−5.573	263
400	0.0031	−5.776	323

Sample calculations for $t = 50$ s:

$$\ln(0.0079) = -4.840$$
$$\frac{1}{0.0079} = 126.6 \approx 127$$

(b) Construct the three plots.

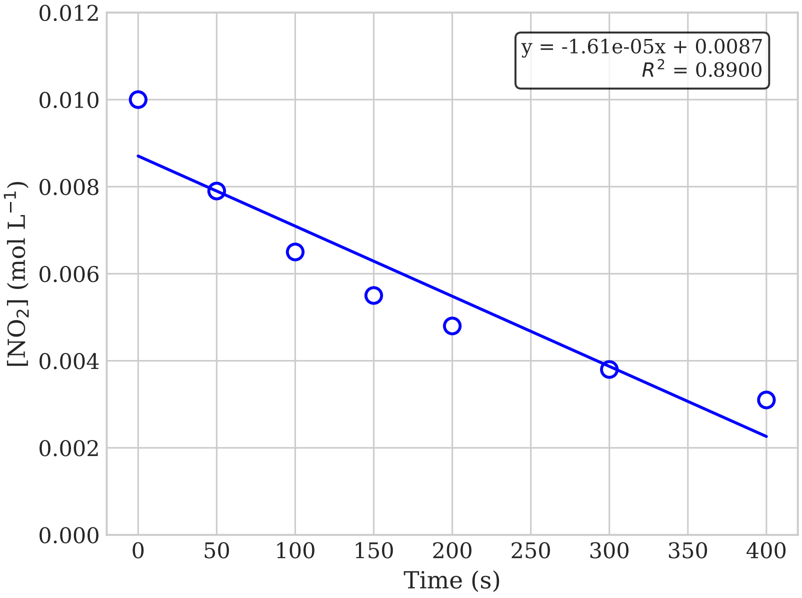

Figure 1: Zero-order test: [NO_2] vs time.

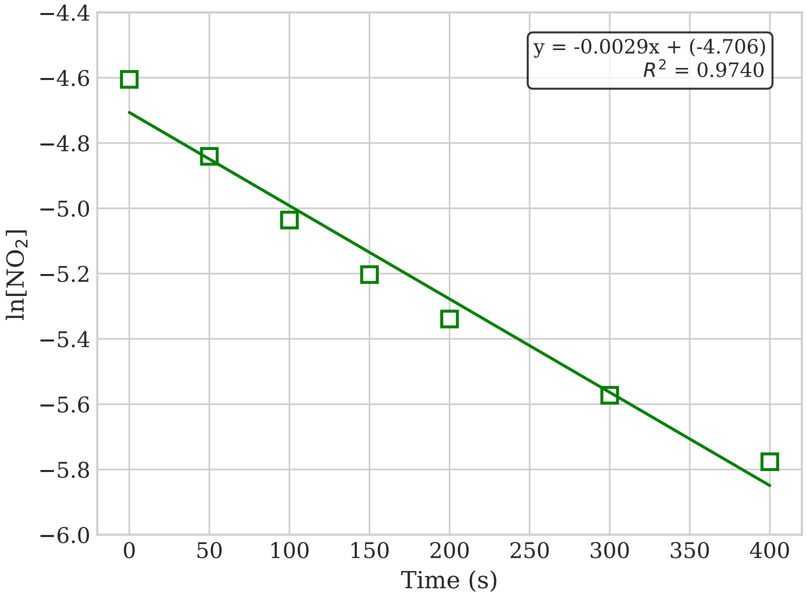

Figure 2: First-order test: ln[NO_2] vs time.

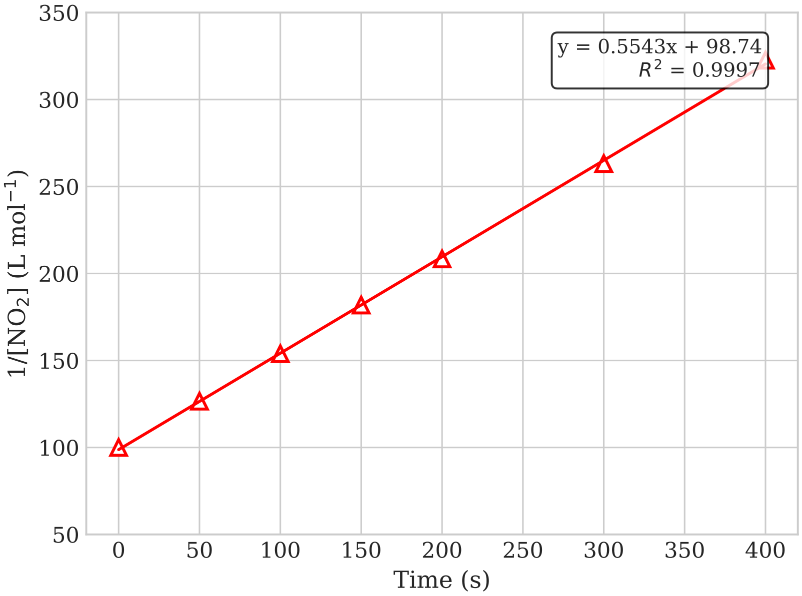

Figure 3: Second-order test: $1/[NO_2]$ vs time.

(c) Identify which plot gives a straight line. What is the order of the reaction?

$$\boxed{\text{Clearly, the plot of } 1/[\mathrm{NO_2}] \text{ vs } t \text{ is the most linear. The reaction is } \textbf{second order}.}$$

Trick! What to do when you cannot plot the data:
Just check in what column the changes with time are constant!

Plot 1: $[\mathbf{NO_2}]$ vs t
Let's check if the decrease is constant (which would indicate zero order):

$$\begin{aligned} \Delta[\mathrm{NO_2}] \text{ from } 0 \to 50 \text{ s}: &\quad 0.0100 - 0.0079 = 0.0021 \\ \Delta[\mathrm{NO_2}] \text{ from } 300 \to 400 \text{ s}: &\quad 0.0038 - 0.0031 = 0.0007 \end{aligned}$$

The changes are **not constant**, so this plot is **curved** → **not zero order**.

Plot 2: $\ln[\mathbf{NO_2}]$ vs t
Let's check if the decrease in $\ln[NO_2]$ is constant:

$$\begin{aligned} \Delta \ln[\mathrm{NO_2}] \text{ from } 0 \to 100 \text{ s}: &\quad -4.605 - (-5.036) = 0.431 \text{ per } 100 \text{ s} \\ \Delta \ln[\mathrm{NO_2}] \text{ from } 200 \to 400 \text{ s}: &\quad -5.340 - (-5.776) = 0.436 \text{ per } 200 \text{ s} = 0.218 \text{ per } 100 \text{ s} \end{aligned}$$

The rate of change is **not constant**, so this plot is **curved** → **not first order**.

Plot 3: $1/[\mathbf{NO_2}]$ vs t
Let's check if the increase in $1/[NO_2]$ is constant:

$$\begin{aligned} \Delta(1/[\mathrm{NO_2}]) \text{ from } 0 \to 100 \text{ s}: &\quad 154 - 100 = 54 \text{ per } 100 \text{ s} \to 0.54 \text{ per s} \\ \Delta(1/[\mathrm{NO_2}]) \text{ from } 100 \to 200 \text{ s}: &\quad 208 - 154 = 54 \text{ per } 100 \text{ s} \to 0.54 \text{ per s} \\ \Delta(1/[\mathrm{NO_2}]) \text{ from } 200 \to 400 \text{ s}: &\quad 323 - 208 = 115 \text{ per } 200 \text{ s} \to 0.575 \text{ per s} \end{aligned}$$

The rate of change is approximately **constant** (≈ 0.55–0.56 per s), so this plot is **linear**.

$$\boxed{\text{The plot of } 1/[\mathrm{NO_2}] \text{ vs } t \text{ is linear. The reaction is } \textbf{second order}.}$$

Exercise 7: Radiometric Dating and the Age of the Earth

Given information:

- Half-life of ^{238}U: $t_{1/2} = 4.468 \cdot 10^9$ years
- Percentage of original ^{238}U remaining: 52.6%

(a) Calculate the decay constant k for ^{238}U in units of year^{-1}.
Step 1: Write the relationship between half-life and decay constant.

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

Step 2: Rearrange to solve for k:

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

Step 3: Substitute the values:

$$k = \frac{0.693}{4.468 \cdot 10^9 \text{ yr}}$$

Step 4: Perform the division:

$$\boxed{k = 1.551 \cdot 10^{-10} \text{ yr}^{-1}}$$

(b) Calculate the age of the zircon crystal.
Step 1: We are told that 52.6% of the original ^{238}U remains. This means:

$$\frac{N}{N_0} = \frac{52.6\%}{100\%} = \frac{52.6}{100} = 0.526$$

where N is the current number of ^{238}U atoms and N_0 is the original number.
Step 2: Write the integrated first-order rate law for radioactive decay:

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

Step 3: Rearrange to solve for t:

$$t = -\frac{\ln(N/N_0)}{k}$$

Step 4: Substitute into the equation:

$$t = -\frac{\ln(0.526)}{1.551 \cdot 10^{-10} \text{ yr}^{-1}} = -\frac{-0.642}{1.551 \cdot 10^{-10} \text{ yr}^{-1}} = \frac{0.642}{1.551 \cdot 10^{-10} \text{ year}^{-1}}$$

Step 5: Perform the division:

$$\boxed{t = 4.14 \cdot 10^9 \text{ yr} \approx 4.1 \text{ billion years}}$$

*(The scientific estimate of Earth's age is nearly **one million times larger** than the traditionally held value based on biblical genealogies.)*

(d) The oldest zircon crystals found on Earth date to approximately 4.4 billion years. What percentage of the original ^{238}U would remain in such a crystal?
Step 1: Write the integrated rate law:

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

Taking the exponential of both sides:

$$\frac{N}{N_0} = e^{-kt}$$

Step 2: Substitute the values:

$$\frac{N}{N_0} = e^{-\left(1.551\cdot 10^{-10}\ \text{yr}^{-1}\right)\times\left(4.4\cdot 10^{9}\ \text{yr}\right)} = e^{-0.682}$$

Step 3: Calculate $e^{-0.682}$:

$$\frac{N}{N_0} = 0.506$$

Step 4: Convert to percentage:

$$\text{Percentage remaining} = 0.506 \times 100\% = 50.6\%$$

$$\boxed{50.6\% \text{ of the original } ^{238}\text{U would remain}}$$

This result makes a lot of sense! The half-life of ^{238}U is 4.468 billion years, and we calculated the remaining uranium after 4.4 billion years.

Since 4.4 billion years is very close to (but slightly less than) one half-life, we expect slightly more than 50% of the original uranium to remain. So this crystal is almost exactly one half-life old.

Exercise 8: The Arrhenius Equation

Reaction: $C_3H_6 \longrightarrow CH_3CH{=}CH_2$ (cyclopropane to propene)

Given data:

Temperature (K)	k (s^{-1})
750	$1.8 \cdot 10^{-4}$
800	$2.7 \cdot 10^{-3}$
850	$3.0 \cdot 10^{-2}$
900	0.26

Key equations:

Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

Logarithmic form:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Two-temperature form:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Gas constant: $R = 8.314\ \text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$

(a) Using the data at $750\,\mathrm{K}$ and $850\,\mathrm{K}$, calculate the activation energy E_a for this reaction.

Step 1: Identify the values:

$$T_1 = 750\text{ K},\quad k_1 = 1.8\cdot 10^{-4}\text{ s}^{-1}$$
$$T_2 = 850\text{ K},\quad k_2 = 3.0\cdot 10^{-2}\text{ s}^{-1}$$

Step 2: Write the two-temperature form of the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Step 3: Substitute into the equation:

$$\ln\left(\frac{3.0\cdot 10^{-2}\text{ s}^{-1}}{1.8\cdot 10^{-4}\text{ s}^{-1}}\right) = \frac{E_a}{8.314\text{ J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}}\left(\frac{1}{750\text{ K}} - \frac{1}{850\text{ K}}\right)$$

$$5.116 = \frac{E_a}{8.314\text{ J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}} \times 1.57\cdot 10^{-4}\text{ K}^{-1}$$

Step 4: Solve for E_a:

$$E_a = \frac{5.116\times 8.314\text{ J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}}{1.57\cdot 10^{-4}\text{ K}^{-1}} = 2.71\cdot 10^{5}\text{ J}\,\mathrm{mol}^{-1}$$

$$\boxed{E_a = 271\text{ kJ}\,\mathrm{mol}^{-1}}$$

(b) Calculate the pre-exponential factor A using your value of E_a and the rate constant at $800\,\mathrm{K}$.

Step 1: Write the logarithmic form of the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Step 2: Rearrange to solve for $\ln A$:

$$\ln A = \ln k + \frac{E_a}{RT} \Rightarrow \ln\left(\frac{A}{k}\right) = \frac{E_a}{RT}$$

Note: We have to put the equation in this way in order to manage the units

Step 3: Substitute the values at $T = 800$ K:

$$k = 2.7\cdot 10^{-3}\text{ s}^{-1}$$
$$E_a = 2.71\cdot 10^{5}\text{ J}\,\mathrm{mol}^{-1}$$
$$R = 8.314\text{ J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$$
$$T = 800\text{ K}$$

$$\ln\left(\frac{A}{2.7\cdot 10^{-3}\text{ s}^{-1}}\right) = \frac{2.71\cdot 10^{5}\text{ J}\,\mathrm{mol}^{-1}}{8.314\text{ J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}\times 800\text{ K}}$$

Step 4: Calculate A:

$$\ln\left(\frac{A}{2.7\cdot 10^{-3}\text{ s}^{-1}}\right) = 40.74$$

$$\left(\frac{A}{2.7 \cdot 10^{-3}\ \mathrm{s}^{-1}}\right) = e^{40.74} \Rightarrow A = e^{40.74} \times 2.7 \cdot 10^{-3}\ \mathrm{s}^{-1}$$

$$\boxed{A = 1.3 \cdot 10^{15}\ \mathrm{s}^{-1}}$$

Remember: A is such a big number because it represents the number of efficient collisions!

(c) Predict the rate constant at 700 K.

Step 1: Use the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

Step 2: Substitute:

$$k_{700\ \mathrm{K}} = 1.3 \cdot 10^{15}\ \mathrm{s}^{-1} e^{\frac{2.71 \cdot 10^5\ \mathrm{J\,mol^{-1}}}{8.314\ \mathrm{J\,mol^{-1}\,K^{-1}} \times 700\ \mathrm{K}}}$$

Step 3: Calculate k:

$$k_{700\ \mathrm{K}} = (1.3 \cdot 10^{15}\ \mathrm{s}^{-1}) \times (5.4 \cdot 10^{-21})$$

$$\boxed{k_{700\ \mathrm{K}} = 7.0 \cdot 10^{-6}\ \mathrm{s}^{-1}}$$

(d) Calculate the half-life at 750 K and 900 K. Comment on the practical implications.

For a first-order reaction, the half-life is:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

At 750 K:
$k_{750} = 1.8 \cdot 10^{-4}\ \mathrm{s}^{-1}$

$$t_{1/2} = \frac{0.693}{1.8 \cdot 10^{-4}\ \mathrm{s}^{-1}} = 3850\ \mathrm{s}$$

$$\boxed{t_{1/2} \text{ at } 750\ \mathrm{K} \approx 64 \text{ minutes}}$$

At 900 K:
$k_{900} = 0.26\ \mathrm{s}^{-1}$

$$t_{1/2} = \frac{0.693}{0.26\ \mathrm{s}^{-1}} = 2.67\ \mathrm{s}$$

$$\boxed{t_{1/2} \text{ at } 900\ \mathrm{K} = 2.67\ \mathrm{s}}$$

Comparison and practical implications:

$$\frac{t_{1/2}(750\ \mathrm{K})}{t_{1/2}(900\ \mathrm{K})} = \frac{3850}{2.67} \approx 1430$$

The half-life decreases by a factor of approximately **1430** when the temperature increases by 150 K. In other words, a reaction that's easy to monitor in the lab becomes much harder to follow in the lab!!!