

# Science Fundamentals 1Y

## Chemical Kinetics Workshop

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18-02-2026

### Exercise 1: Determining Reaction Stoichiometry from Reaction Rates

In a chemical reaction, the rates of consumption and formation of species are related to the stoichiometric coefficients. For a general reaction:



the relationship between rates is:

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

**Problem:** In an experiment studying an unknown reaction, the following instantaneous rates were measured at a particular moment:

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

- Identify which species are reactants and which are products.
- Determine the stoichiometric coefficients of the balanced equation.
- Write the balanced chemical equation.
- Calculate the overall reaction rate.

### Exercise 2: The Beer–Lambert Law

The Beer–Lambert law relates the absorbance of a solution to its concentration:

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

where  $A$  is the absorbance (dimensionless),  $\varepsilon$  is the molar absorption coefficient ( $\text{L mol}^{-1} \text{cm}^{-1}$ ),  $l$  is the path length (cm), and  $c$  is the concentration ( $\text{mol L}^{-1}$ ).

**Problem:** A kinetic study monitors the decomposition of a coloured compound X by UV-Vis spectroscopy. The molar absorption coefficient of X at 520 nm is  $\varepsilon = 1.25 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$ . A 1.00 cm cuvette is used.

- (a) A freshly prepared solution of X shows an absorbance of  $A = 0.875$ . Calculate the initial concentration of X.
- (b) After 10 min, the absorbance has decreased to  $A = 0.625$ . What is the concentration of X at this time?

### Exercise 3: Calculating Average Reaction Rates

The average rate of a reaction over a time interval is defined as:

$$\text{Average rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = -\frac{[\text{Reactant}]_2 - [\text{Reactant}]_1}{t_2 - t_1}$$

**Problem:** The concentration of a reactant A was monitored during a reaction, yielding the following data:

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

- (a) Calculate the average rate of disappearance of A over the interval  $t = 0$  s to  $t = 20$  s.
- (b) Calculate the average rate over the interval  $t = 80$  s to  $t = 100$  s.
- (c) Compare your answers to (a) and (b). Explain why they differ.
- (d) Calculate the average rate over the entire experiment ( $t = 0$  s to  $t = 100$  s).
- (e) Why is the instantaneous rate generally more useful than the average rate in kinetic studies?

### Exercise 4: Identifying Reaction Orders from Rate Laws

The rate law for a reaction has the general form:

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

where  $m$ ,  $n$ ,  $p$ , ... are the orders with respect to each reactant, and the overall order is the sum of all individual orders.

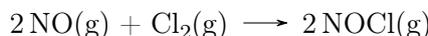
**Problem:** For each of the following rate laws, identify: (i) the order with respect to each reactant, and (ii) the overall reaction order. Also, determine the units of the rate constant  $k$  assuming concentrations are in  $\text{mol L}^{-1}$  and time is in s.

- (a)  $r = k[\text{NO}]^2[\text{O}_2]$
- (b)  $r = k[\text{H}_2\text{O}_2]$
- (c)  $r = k[\text{NO}]^2[\text{Cl}_2]$
- (d)  $r = k$  (for the decomposition of  $\text{NH}_3$  on a tungsten surface)

## Exercise 5: Determining Reaction Orders and Rate Constants

The method of initial rates uses data from the beginning of a reaction (where concentrations haven't changed significantly) to determine the rate law.

**Problem:** The reaction between nitrogen monoxide and chlorine:



was studied at 300 K. The following initial rate data were obtained:

Experiment	[NO] (mol L <sup>-1</sup> )	[Cl <sub>2</sub> ] (mol L <sup>-1</sup> )	Initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.010	0.010	$1.2 \times 10^{-4}$
2	0.010	0.020	$2.4 \times 10^{-4}$
3	0.020	0.020	$9.6 \times 10^{-4}$

- Determine the order of the reaction with respect to NO.
- Determine the order of the reaction with respect to Cl<sub>2</sub>.
- Write the rate law for this reaction.
- Calculate the value of the rate constant  $k$ , including its units.
- Using your rate law, predict the initial rate when [NO] = 0.015 mol L<sup>-1</sup> and [Cl<sub>2</sub>] = 0.025 mol L<sup>-1</sup>.

## Exercise 6: Graphical Determination of Reaction Order

The integrated rate laws for reactions of different orders give linear plots when the appropriate function of concentration is plotted against time:

Order	Integrated rate law	Linear plot
0	$[A] = [A]_0 - kt$	[A] vs $t$
1	$A = [A]_0 e^{-kt}$	ln[A] vs $t$
2	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]}$ vs $t$

**Problem:** The decomposition of nitrogen dioxide:



was studied at 500 K. The following concentration data were recorded:

Time (s)	[NO <sub>2</sub> ] (mol L <sup>-1</sup> )	ln[NO <sub>2</sub> ]	1/[NO <sub>2</sub> ] (L mol <sup>-1</sup> )
0	0.0100		
50	0.0079		
100	0.0065		
150	0.0055		
200	0.0048		
300	0.0038		
400	0.0031		

- Complete the table by calculating ln[NO<sub>2</sub>] and 1/[NO<sub>2</sub>] for each time point.

(b) Please make these three plots:

- $[\text{NO}_2]$  versus time
- $\ln[\text{NO}_2]$  versus time
- $1/[\text{NO}_2]$  versus time

(c) What is the order of the reaction?

## Exercise 7: Radiometric Dating and the Age of the Earth

Radioactive decay follows first-order kinetics. The half-life ( $t_{1/2}$ ) is the time required for half of the radioactive nuclei to decay:

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

**Background:** For centuries, estimates of Earth's age were based on biblical genealogies, with a commonly cited value of approximately 4,500 years (famously calculated by Archbishop James Ussher in 1650 as 4004 BC). The discovery of radioactivity in the late 19th century revolutionised our understanding.

Uranium-238 decays to lead-206 through a series of steps with an overall half-life of  $t_{1/2} = 4.468 \times 10^9$  years. Zircon crystals ( $\text{ZrSiO}_4$ ) are particularly useful for dating the early Earth because they are extremely resistant to weathering and metamorphism, preserving their isotopic composition over billions of years. Crucially, zircon incorporates uranium into its crystal structure when it forms, but strongly excludes lead. This means that any  $^{206}\text{Pb}$  found in a zircon crystal today must have come from radioactive decay of  $^{238}\text{U}$  after the crystal formed. The oldest zircon crystals, found in the Jack Hills of Western Australia, provide a minimum age for the Earth and evidence of solid crust formation in the early Hadean eon.

**Problem:** A zircon crystal from the Jack Hills was analysed. Isotopic analysis revealed that only 52.6% of the original  $^{238}\text{U}$  remains in the crystal.

- Calculate the decay constant  $k$  for  $^{238}\text{U}$  in units of  $\text{year}^{-1}$ .
- Calculate the age of the zircon crystal.
- The oldest zircon crystals found on Earth date to approximately 4.4 billion years. What percentage of the original  $^{238}\text{U}$  would remain in such a crystal?

## Exercise 8: The Arrhenius Equation

The temperature dependence of rate constants is described by the Arrhenius equation:

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

where  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $T$  is the absolute temperature.

The logarithmic form is:

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

For two temperatures:

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

**Problem:** The rate constant for the first-order decomposition of cyclopropane to propene:



was measured at several temperatures:

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

- (a) Using the data at 750 K and 850 K, calculate the activation energy  $E_a$  for this reaction.
- (b) Calculate the frequency factor  $A$  using your value of  $E_a$  and the rate constant at 800 K.
- (c) Predict the rate constant at 700 K.
- (d) The half-life for a first-order reaction is  $t_{1/2} = \ln 2/k$ . Calculate the half-life at 750 K and 900 K. Comment on the practical implications.