

Session 3 – Chemical Kinetics, Decomposition and Thermal Stability

Lifecycle focus: Storage → Use

Central question:

*How quickly does an energetic material change,
and how does temperature affect its lifetime
and behaviour?*



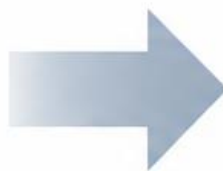
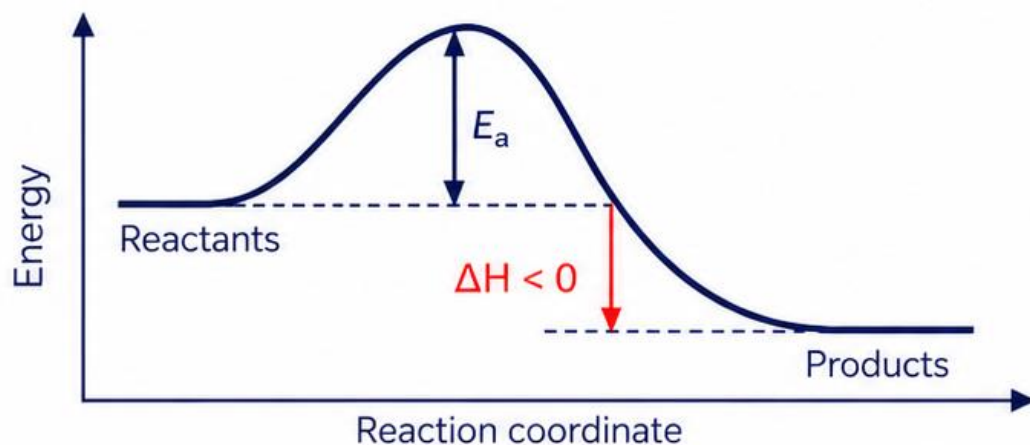
From Session 2 to Session 3

Session 2

How much energy?

Reaction energies and thermochemistry

- Enthalpy and internal energy (ΔH , ΔU)
- Heat and work in chemical reactions
- Energy released by decomposition reactions

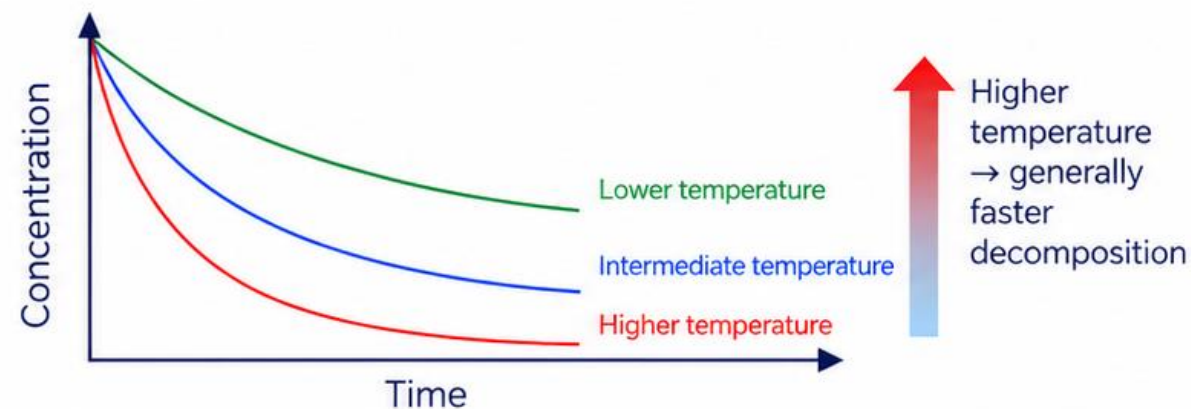


Session 3

How fast?

Chemical kinetics, decomposition and thermal stability

- Experimental kinetics and kinetic models
- Temperature dependence and Arrhenius analysis
- Complex decomposition and chemical stability
- Ageing and lifetime prediction



Session 3 – Learning Outcomes

By the end of this session you should be able to:

1

Explain how **reaction kinetics** describes the **rate** of chemical reactions, and write and interpret rate laws and simple kinetic models.

2

Analyse the **effect of temperature** on reaction rates using the Arrhenius equation, and interpret Arrhenius plots and activation energies.

3

Discuss **decomposition pathways** and the factors affecting **thermal stability**, including the role of stabilisers and impurities, in energetic materials.

4

Apply kinetic and thermal stability concepts to the **storage and use** of energetic materials, and critically evaluate the **implications and limitations** of experimental findings for safety, performance and lifetime.

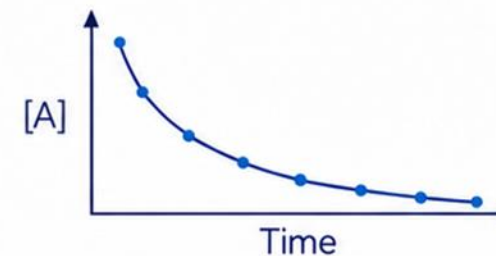
Session 3 – Today's Roadmap

Teaching blocks

1

How do we investigate reaction kinetics?

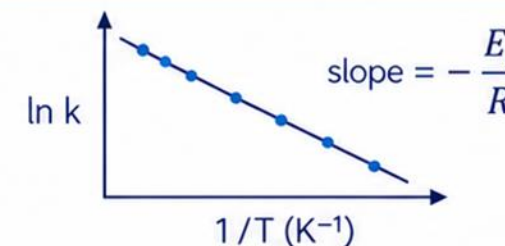
- Experimental measurements and rate laws
- Kinetic model selection and evaluation
- Model versus molecular mechanism



2

How do we interpret temperature dependence?

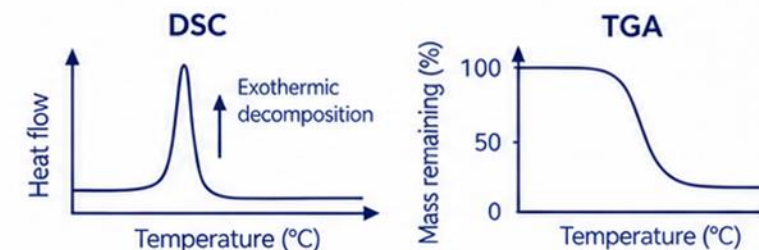
- Arrhenius analysis and kinetic parameters
- Predicting changes in reaction rate
- Assumptions and limitations



3

How does decomposition affect chemical stability?

- Complex decomposition and autocatalysis
- Experimental evidence: DSC, TGA, HPLC and HFC
- Stabilisers, chemical ageing and limits of lifetime prediction.



Application activity

4

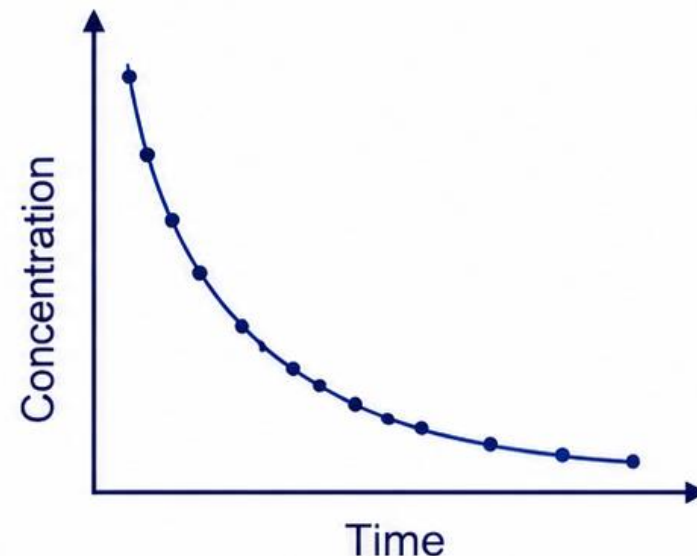
Applying the chemistry

- Practical 2: experimental reaction kinetics
- Presentation activity: Claim $\rightarrow$ Chemistry $\rightarrow$ Evidence $\rightarrow$ Lifecycle significance $\rightarrow$ Limitation

BLOCK 1 – EXPERIMENTAL KINETICS AND KINETIC MODELS

How do we investigate reaction kinetics?

From experimental measurements to kinetic models to understand how quickly energetic materials change.



Reaction Kinetics – What Do We Already Know?

Consider the following experimentally determined rate law:

$$rate = k[A]^2[B]$$

1

What does the rate constant k represent, and what are its units for this reaction?

2

What is the reaction order with respect to A and B? What is the overall reaction order?

3

If the concentration of A doubles (while [B] remains constant), how does the reaction rate change?

4

If the concentrations of both A and B double, by what factor does the reaction rate change?

Reaction Kinetics – Answers

For the experimentally determined rate law:

$$rate = k[A]^2[B]$$

Question	Answer	Explanation
1 What does the rate constant k represent, and what are its units?	Rate constant $L^2 \text{ mol}^{-2} \text{ s}^{-1}$	Constant at a given temperature and fixed conditions.
2 What are the orders with respect to A and B? What is the overall order?	A: 2 B: 1 Overall: 3	Orders are given by the exponents in the rate law. Overall order = 2 + 1.
3 If $[A]$ doubles (while $[B]$ remains constant), how does the rate change?	Increases fourfold ($\times 4$).	$rate \propto [A]^2$. Doubling $[A]$ gives $2^2 = 4$.
4 If both $[A]$ and $[B]$ double, by what factor does the rate change?	Increases eightfold ($\times 8$).	$rate = k[A]^2[B]$. Doubling both gives $2^2 \times 2 = 8$.

Reaction order vs stoichiometry

- Orders (2 and 1) are determined experimentally.
- They are not usually the same as the stoichiometric coefficients.

Does this rate law prove the mechanism?

- No.
- A rate law constrains possible mechanisms, but does not uniquely define the molecular steps.

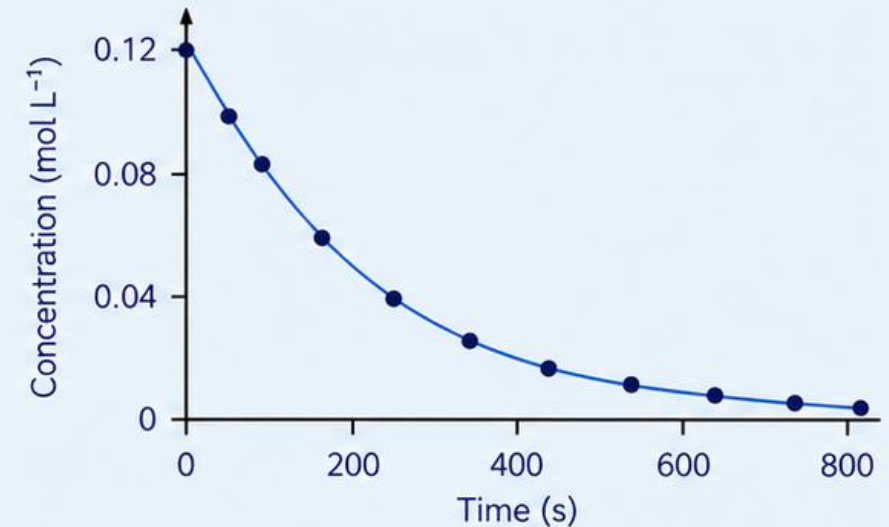
Determining Reaction Order – Why Does It Matter?

Reaction order tells us how strongly the measured reaction rate depends on reactant concentration.

Determining the reaction order allows us to:

- **Understand reaction behaviour:** identify which species influence the rate.
- **Predict rate changes:** estimate how the reaction responds when concentrations change (e.g. dilution, mixing, stabiliser concentration).
- **Evaluate kinetic models:** use experimental evidence to test whether a proposed rate law describes the reaction.

Example: first-order kinetics



OME connection

Knowing the reaction order helps us:

- predict how decomposition rates change during storage and use,
- interpret experimental stability data, and
- support interpretation of stabiliser-depletion and degradation kinetics.

We determine reaction order to support prediction, interpretation and lifecycle decisions — not just to perform calculations.

How Do We Measure Reaction Rate Experimentally?

1

Prepare reaction mixtures

- Use known initial concentrations.
- Keep temperature and other conditions constant.

2

Measure concentration change with time

- Follow the disappearance of a reactant or formation of a product.
- Use a suitable analytical method (e.g. UV-Vis, HPLC, GC).

3

Determine the initial rate

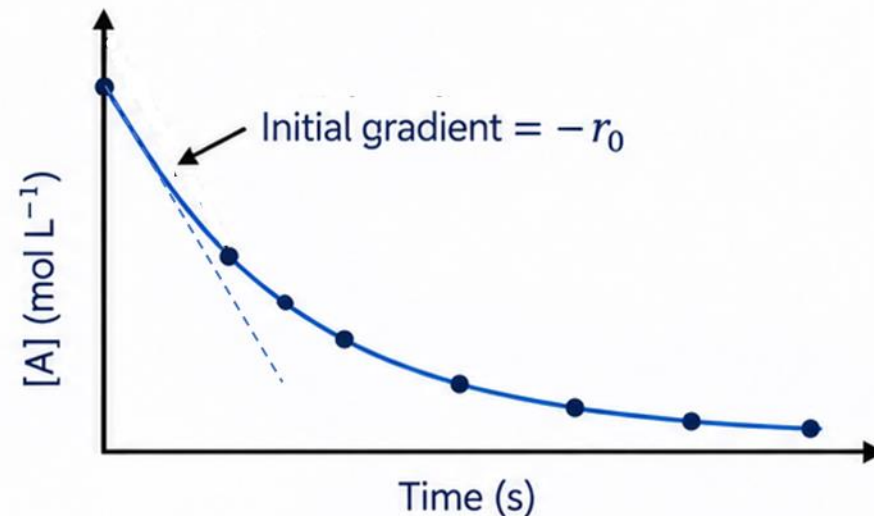
- Obtain a concentration–time profile.
- The initial rate is the slope at the start of the reaction:

$$r_0 = - \left. \frac{d[A]}{dt} \right|_{t=0}$$

4

Repeat with different initial concentrations

- Vary one reactant concentration at a time.
- Compare the initial rates to determine the reaction order(s).



Key points

- The initial rate is measured at very short times to minimise changes in concentration.
- Initial rates are used to determine the reaction order(s) and rate law.
- Temperature, solvent, catalyst and other conditions should be kept constant.

Initial-rate measurements provide the experimental evidence used to establish a rate law and evaluate kinetic models.

Determining Reaction Order from Experimental Data

Key idea: compare experiments in which only one reactant concentration changes at a time.

Reaction under study: $A + B \rightarrow \text{products}$

From the experimental data: $rate = k[A]^2[B]$

Experiment	[A] / mol L ⁻¹	[B] / mol L ⁻¹	Initial rate / mol L ⁻¹ s ⁻¹
1	0.10	0.10	0.0020
2	0.20	0.10	0.0080
3	0.10	0.20	0.0040

How to interpret the data

Step 1 – Compare experiments 1 and 2

- [A] doubles while [B] remains constant.
- Initial rate increases by a factor of 4 ($\times 4$).
- Therefore, the order with respect to A is 2 ($m = 2$).

Step 2 – Compare experiments 1 and 3

- [B] doubles while [A] remains constant.
- Initial rate increases by a factor of 2 ($\times 2$).
- Therefore, the order with respect to B is 1 ($n = 1$).

Step 3 – Write the rate law

- $rate = k[A]^2[B]$ (overall order = 3).

Key takeaway: Reaction order is determined from experimental evidence, not directly from the balanced chemical equation.

Zero-Order Reaction Model

Model and equations

Rate law: $\text{rate} = k$

Integrated form: $[A] = [A]_0 - kt$

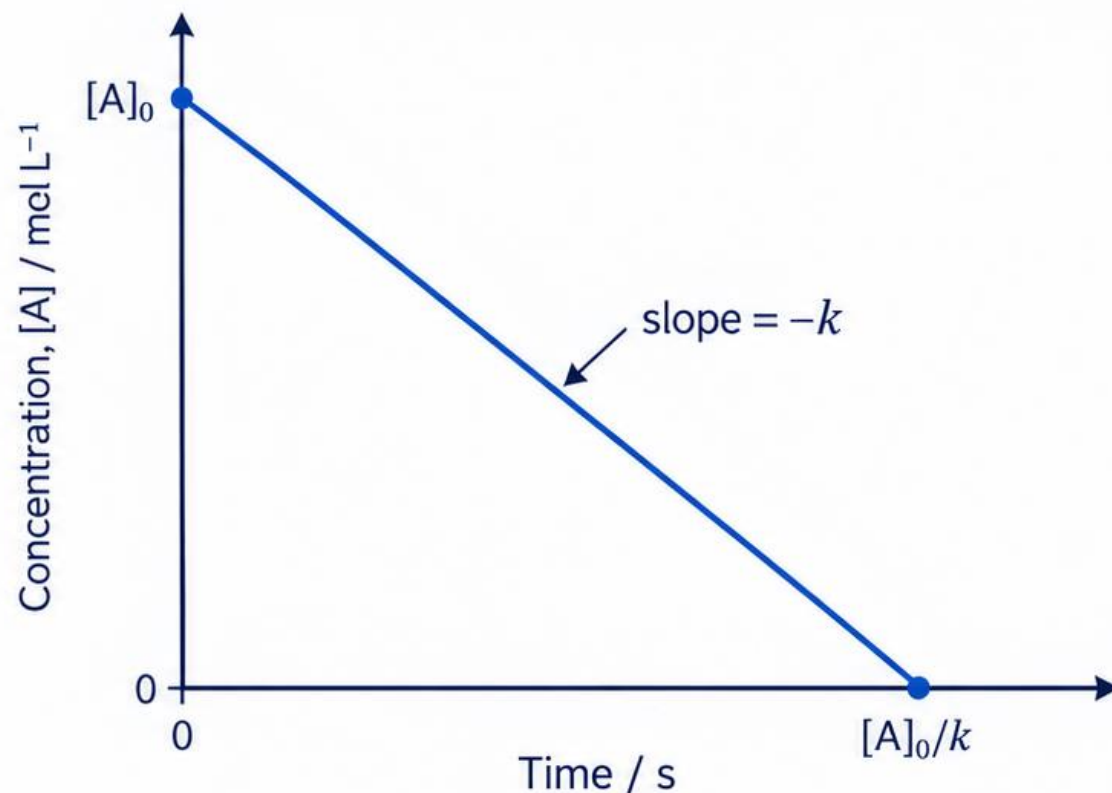
For zero-order kinetics, k has units of concentration $\times$ time⁻¹ (e.g. mol L⁻¹ s⁻¹).

Half-life: $t_{1/2} = \frac{[A]_0}{2k}$

Key features

- Rate is independent of reactant concentration.
- $[A]$ vs t is linear.
- Slope = $-k$.
- Half-life depends on the initial concentration.

Characteristic zero-order plot



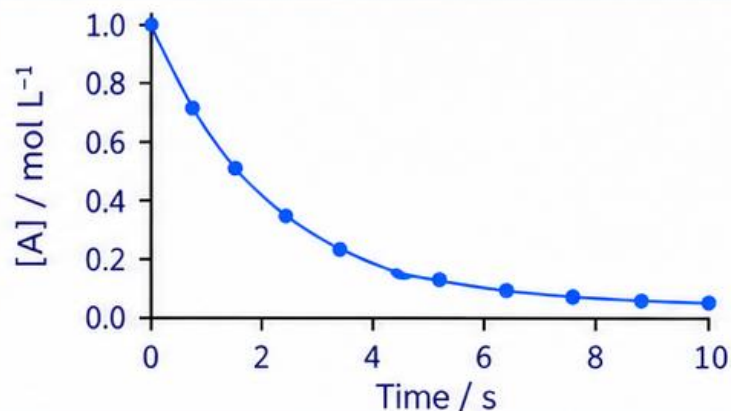
A zero-order model describes a process that proceeds at a constant rate under the conditions studied.



Identifying a First-Order Kinetic Model

The same concentration–time data can be tested using different integrated rate-law plots.

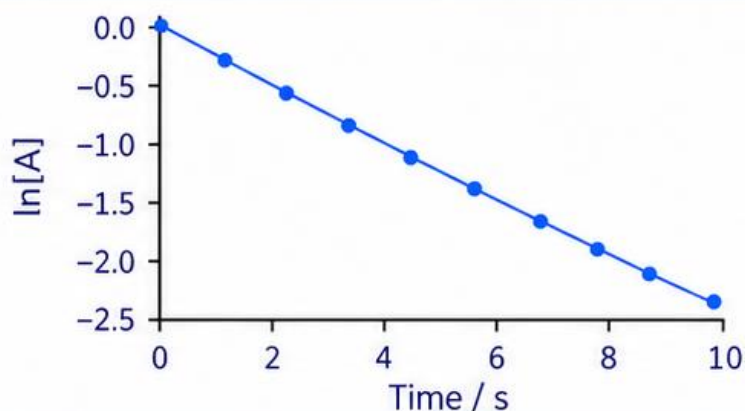
[A] vs t (zero order)



Not linear

Zero-order model not appropriate.

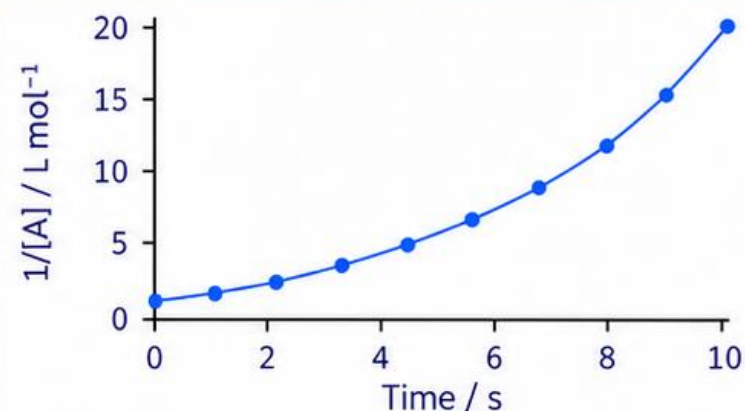
$\ln[A]$ vs t (first order)



Linear

First-order model is most appropriate.

$1/[A]$ vs t (second order)



Not linear

Second-order model not appropriate.

What does this mean?

- Each integrated rate law gives a different linear plot.
- A linear relationship indicates a suitable kinetic model.
- Here, $\ln[A]$ vs t is linear, so the data are consistent with first-order kinetics.
- The gradient of the straight line is $-k$ (for a first-order reaction).

Key points

- The same experimental dataset has been used for all three plots.
- A straight line suggests the corresponding kinetic model is appropriate.
- Use $\ln[A]$ for graphical testing (commonly used at this level).
- The straightest plot is not by itself proof of the correct model — always check the quality of fit and the residuals.

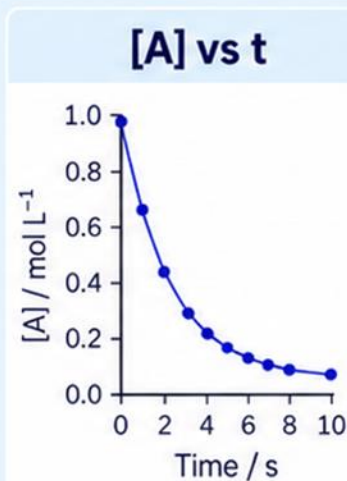
Linear plots help identify candidate kinetic models; their reliability must be checked against experimental data.



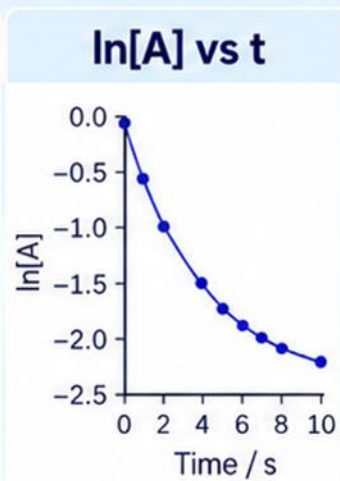
Second-Order Kinetics — How Does Concentration Affect the Rate?

Second-order model

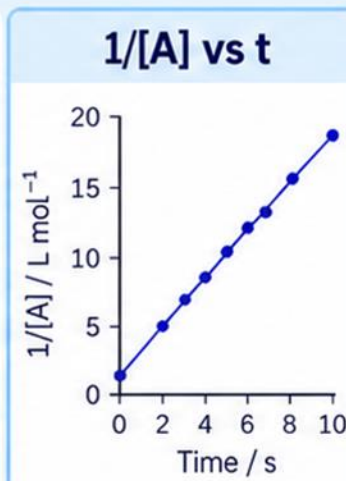
- Rate law: $\text{rate} = k[A]^2$
- Integrated law:
 $1/[A] = 1/[A]_0 + kt$
- Linear plot: $1/[A]$ vs t
- Slope = $+k$
- Units of k : $\text{L mol}^{-1} \text{s}^{-1}$



Not linear
Zero-order model
not appropriate.



Not linear
First-order model
not appropriate.



Linear
Second-order model
is most appropriate.

Key implications

- Doubling $[A]$ increases the rate fourfold.
- Half-life depends on the initial concentration: $t_{1/2} = 1/(k[A]_0)$.
- Second-order kinetics show a stronger concentration dependence than first-order kinetics.
- A linear reciprocal-concentration plot supports the model, but does not prove the molecular mechanism.

Key takeaway: second-order kinetics are identified by a linear plot of $1/[A]$ against time, but the model must still be checked against data quality and residuals.

First-Order Half-Life

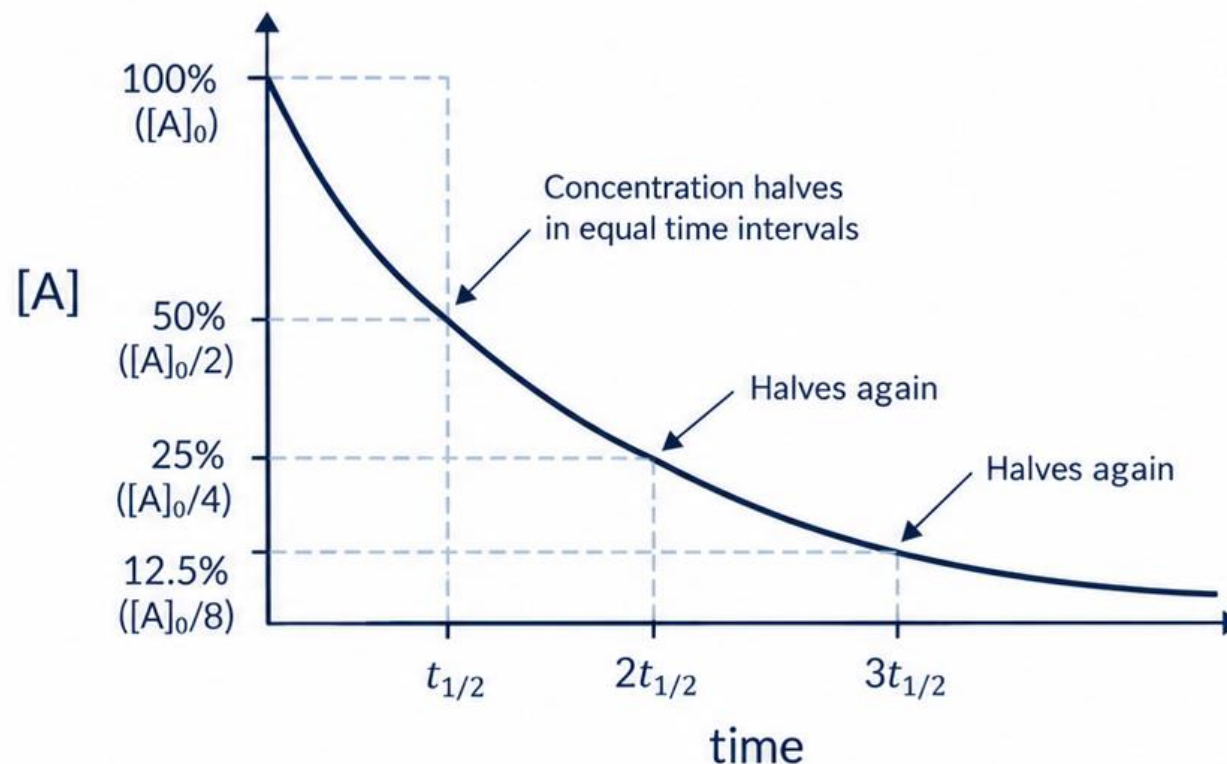
Half-life ($t_{1/2}$) is the time required for the concentration of a reactant to decrease to half its initial value.

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

For first-order kinetics, k has units of time^{-1} (for example s^{-1}).

- Larger $k \rightarrow$ shorter half-life
- Smaller $k \rightarrow$ longer half-life
- For a first-order reaction, half-life is independent of the initial concentration

Important: kinetic half-life does not automatically equal safe storage life or service life.



What Do Kinetic Parameters Actually Tell Us?

Reaction order

- Shows how the measured rate depends on concentration.
- Is determined experimentally from kinetic data.
- Does not by itself prove the molecular mechanism.

Rate constant, k

- Quantifies the rate–concentration relationship for a specified model.
- Larger k generally means faster reaction only when comparing the same kinetic model under the same conditions.
- Its units depend on the overall reaction order.
- Its value depends on temperature and reaction conditions.

Kinetic parameters describe observed reaction behaviour under defined conditions.

Important: kinetic parameters are model-dependent and condition-dependent.

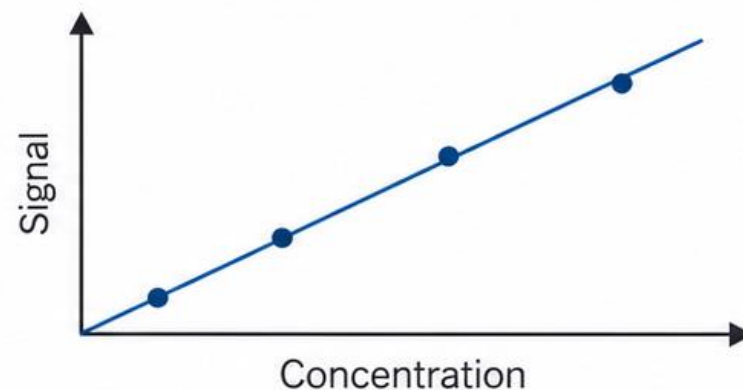
How Are Concentrations Measured Experimentally?

Common approaches

- **Direct chemical analysis:** sampling and measuring reactant or product concentration.
- **Spectroscopic methods:** convert absorbance or another signal into concentration.
- **Chromatographic methods:** use techniques such as HPLC or GC to quantify chemical species.
- **Other measurable signals:** pressure, conductivity or mass can sometimes be related to concentration.

From signal to concentration

1. Measure a signal that changes during the reaction.
2. Use calibration or a known relationship to convert signal to concentration.
3. Construct concentration–time data for kinetic analysis.



Important: kinetic conclusions depend on the quality, calibration and time resolution of the measurements.

What Makes a Kinetic Model Reliable?

Four questions to ask

1. Quality of fit:

Does the model describe the measurements across the full experimental range?

2. Residuals:

Are the differences between measured and predicted values small and randomly distributed?

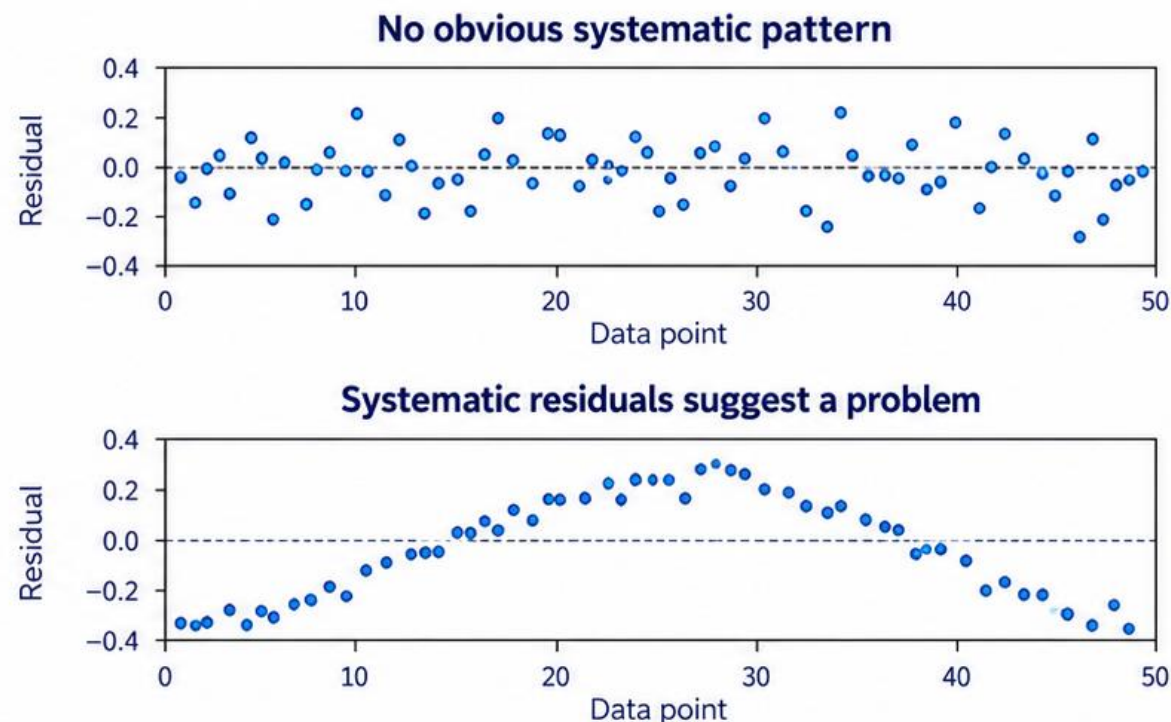
3. Reproducibility:

Do repeated measurements give consistent results?

4. Validity:

Does the model remain appropriate under the conditions being studied?

Checking the evidence



A good fit supports a kinetic model, but it does not by itself prove the molecular mechanism.

Reliable kinetic interpretation depends on both the quality of the data and the suitability of the model.

Does a Rate Law Reveal the Reaction Mechanism?

Reaction under study: $A + B \rightarrow \text{products}$

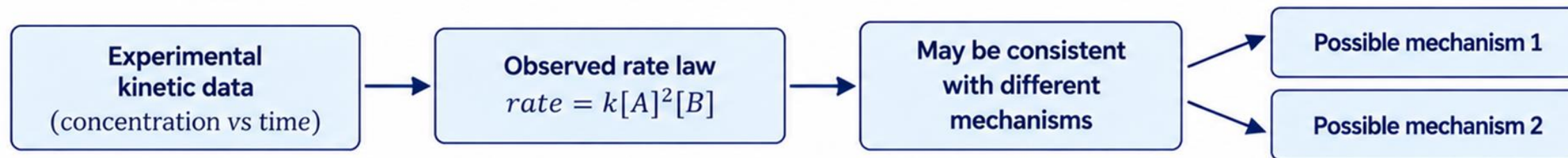
Experimentally determined rate law: $\text{rate} = k[A]^2[B]$

What the rate law tells us

- Which species affect the rate and their reaction orders (second order in A, first order in B).
- How the rate changes when concentrations change.
- It can be used to make predictions within the experimental conditions over which it was determined.

What the rate law does not tell us

- The number of elementary reaction steps.
- The identity or structure of reaction intermediates.
- The complete molecular mechanism.
- It cannot distinguish between different mechanisms that give the same rate law.



A rate law is experimental evidence, not proof of a unique molecular mechanism.

Rate Law versus Elementary Reaction

Overall reaction (measured experimentally)

- The rate law describes the **experimentally observed** relationship between rate and concentration.
- Reaction orders are determined from kinetic data.
- They do not necessarily match the stoichiometric coefficients in the balanced equation.

Example: decomposition of dinitrogen pentoxide



Observed rate law: $rate = k[\text{N}_2\text{O}_5]$

The reaction is first order in N_2O_5 , even though the stoichiometric coefficient is 2.

Elementary reaction (single molecular step)

- An elementary step involves one specific molecular event.
- For elementary reactions, the rate law follows the **molecularity** of that step (mass-action kinetics).
- The crude stoichiometric coefficients equal the rate-law exponents for that elementary step.

Example: elementary bimolecular reaction



Rate law: $rate = k[\text{NO}][\text{O}_3]$

This is a single-step, bimolecular reaction, so the rate is first order in NO and first order in O_3 .

Key point: The form of a rate law provides information about kinetic behaviour, but does not by itself reveal the overall mechanism of a reaction.

Why Can a Reaction Show an Apparent Reaction Order?

Key idea

The observed reaction order describes measured kinetic behaviour under specific conditions. It does not always reveal the full underlying reaction law or molecular mechanism.

Common reason: one reactant is in large excess

$$\text{rate} = k[A][B]$$

If $[B]$ changes very little, then $[B] \approx \text{constant}$

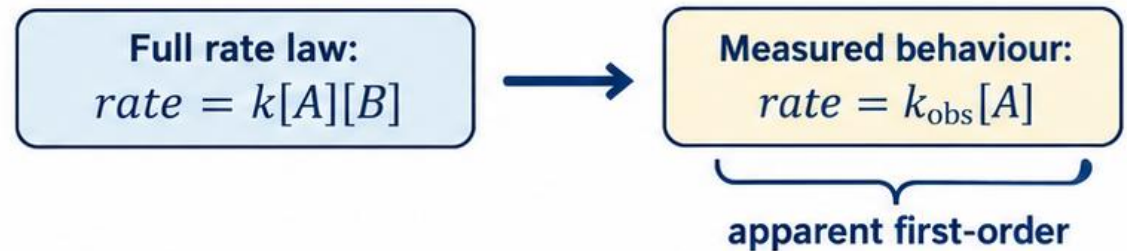
$$\text{rate} = k_{\text{obs}}[A]$$

$$\text{where } k_{\text{obs}} = k[B]$$

The reaction shows pseudo-first-order behaviour with respect to A under these conditions.

What does this mean?

- The apparent order depends on the experimental conditions.
- A complex or multistep reaction may still produce a simple observed rate law.
- In heterogeneous or solid systems, the measured rate may also reflect diffusion, interfaces or changing material structure.
- Observed order supports kinetic interpretation, but does not by itself prove the molecular mechanism.



Observed reaction order can be apparent: it reflects how the reaction behaves under the conditions studied.

Why Do We Start with Solution Kinetics?

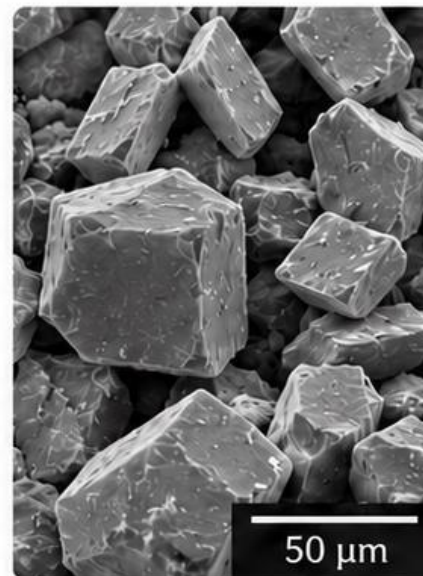
Solution reactions provide a simpler, well-controlled system to study the fundamental principles of chemical kinetics, which can then be applied to understand more complex solid systems.

Solution kinetics



- Reactants can be uniformly mixed and measured.
- Concentrations are controlled and quantified (e.g. UV-Vis, HPLC, GC).
- Rate can be studied under well-defined conditions.
- Rate law: $rate = k[A]^n$

Energetic solids and formulations



- Reactants may be non-uniformly mixed (particles, interfaces).
- Reactions can occur within particles, at surfaces or interfaces.
- Diffusion, heat transfer and phase changes may influence the observed rate.
- Kinetic behaviour is often described using conversion or other measurable properties.

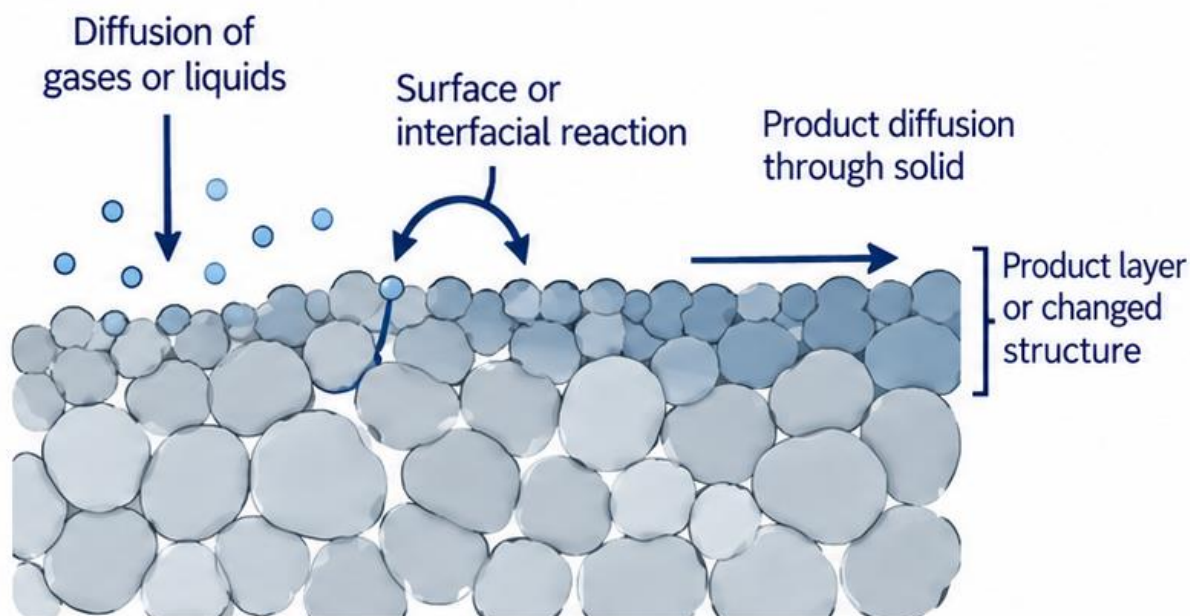
The experimental principles developed using solution kinetics provide a foundation that can be adapted to study more complex solid systems.

How Do Reaction Kinetics Relate to Solid Materials?

Why are solid materials different?

- Reactants may not be uniformly mixed.
- Reactions can occur **within the bulk material**, at **surfaces** or at **interfaces**.
- Diffusion of gases or liquids can **limit** the observed rate.
- Particle size, morphology and contact between components can **change** the rate.
- Heat transfer, temperature gradients and phase or structural changes may also **influence** the kinetics.

Illustrative processes in a solid material



Key point: In solid and heterogeneous materials, the observed kinetics may reflect both chemical reaction and physical processes, depending on the material and conditions.

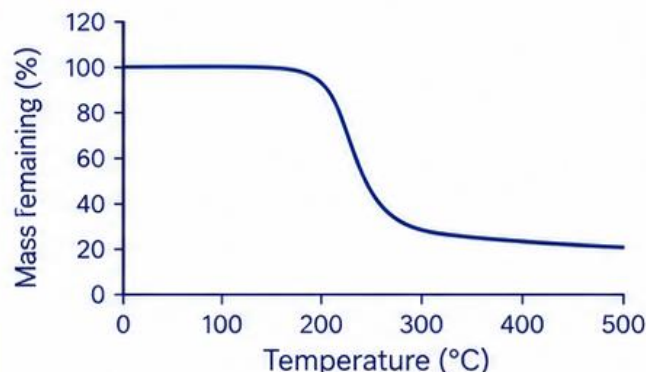
How Do We Measure Decomposition in Energetic Materials?

Gas evolution



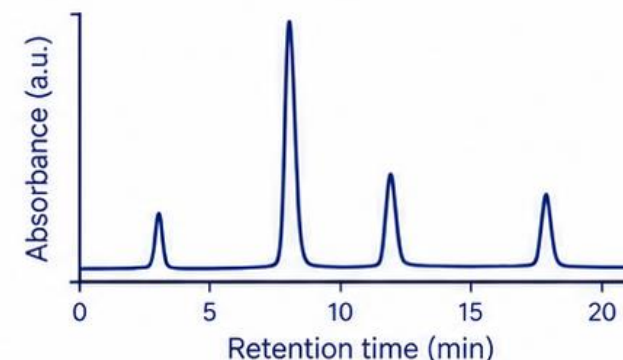
- Measure the volume or pressure of gas released with time.
- Provides information about gas-generation kinetics.
- The measured gas may include several species and does not necessarily correspond to a single decomposition step.

TGA



- Measure the sample mass as a function of temperature (or time).
- Reveals mass-loss behaviour during decomposition, evaporation or sublimation.
- Mass loss does not always prove chemical decomposition.

HPLC



- Separate and quantify selected chemical species.
- Measure concentrations using calibration (peak area).
- Useful for monitoring reactant depletion, stabiliser consumption or product formation.

Key point: Different techniques measure different observables (gas generation, mass loss or chemical concentration) which are not automatically the same as the chemical rate of a specific reaction.

Why Does Kinetic Behaviour Matter Across the OME Lifecycle?

Storage → Use

During storage

- Slow chemical change
- Investigate decomposition, stabiliser depletion and ageing
- Aim: maintain chemical stability over time



During intended use

- Rapid energetic reaction
- Investigate ignition, combustion or detonation behaviour
- Aim: deliver the required functional performance

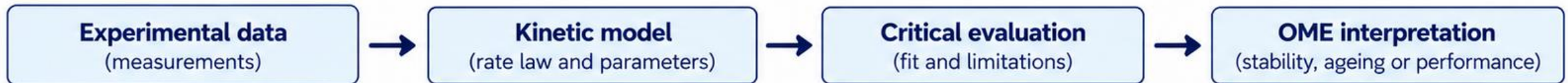


A kinetic model describing slow storage decomposition cannot automatically be used to describe rapid reaction behaviour during use.

Different lifecycle stages may involve different dominant reaction pathways and different kinetic behaviour.

Experimental Kinetics: Key Takeaways

- 1 Reaction order and rate constant**
 - Determined from experimental concentration–time data.
 - Show how the reaction rate depends on reactant concentration.
- 2 Kinetic models**
 - Use the data to identify a suitable model (e.g. zero, first or second order).
 - Model parameters (e.g. k) are obtained from the fitted data.
- 3 Model versus mechanism**
 - A kinetic model describes the observed behaviour.
 - It does not necessarily reveal the molecular reaction mechanism.
- 4 Application to energetic materials**
 - Measurements may reflect chemical and physical processes.
 - Kinetic models from simple solutions may not directly apply to energetic solids.

**Key point:**

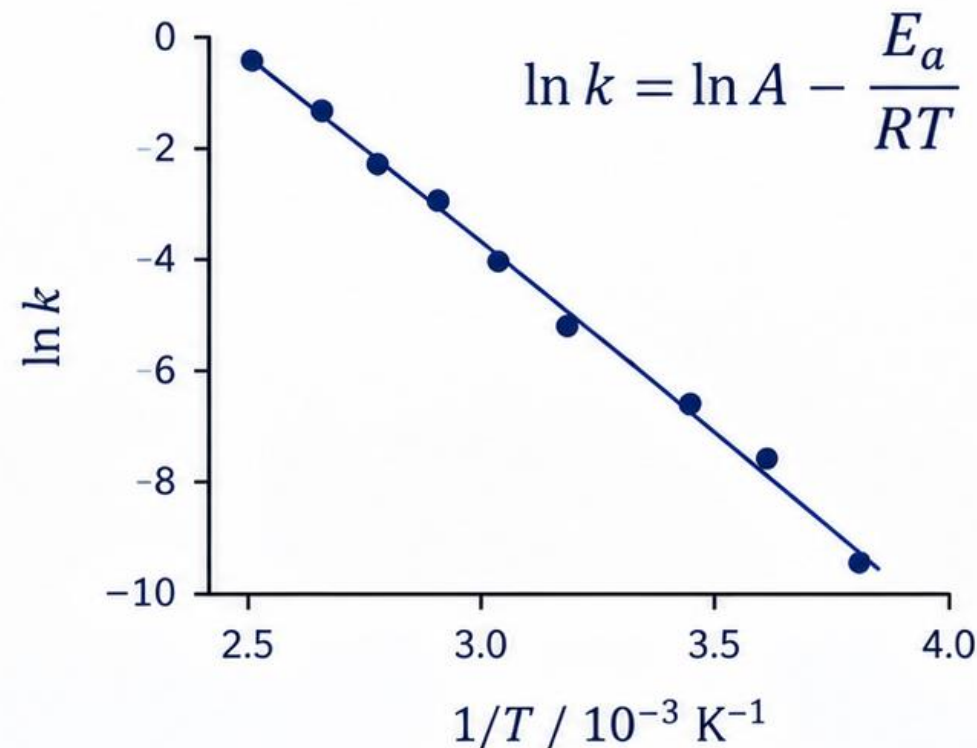
Experimental kinetics provide models for reaction behaviour, but the measured kinetics and their interpretation depend on the material and the conditions.



How Do We Interpret Temperature Dependence?

From experimental rate constants to activation energy, temperature-dependent predictions and their limitations.

- 1 Understand what activation energy represents and how it is determined experimentally.
- 2 Learn to construct and interpret Arrhenius plots and extract kinetic parameters.
- 3 Use kinetic parameters to predict the effect of temperature on reaction rate.
- 4 Evaluate the limitations of Arrhenius analysis, particularly for complex energetic materials.



Arrhenius Equation — What Do We Already Know?

$$k = A e^{-\frac{E_a}{RT}}$$

- 1 What do k , A , E_a and T represent?
- 2 What generally happens to the rate constant, k , when temperature increases, assuming A and E_a remain constant and $E_a > 0$?
- 3 What does a higher activation energy, E_a , tell us about the temperature dependence of k ?
- 4 Does a higher activation energy necessarily mean an energetic material is safer or more chemically stable?

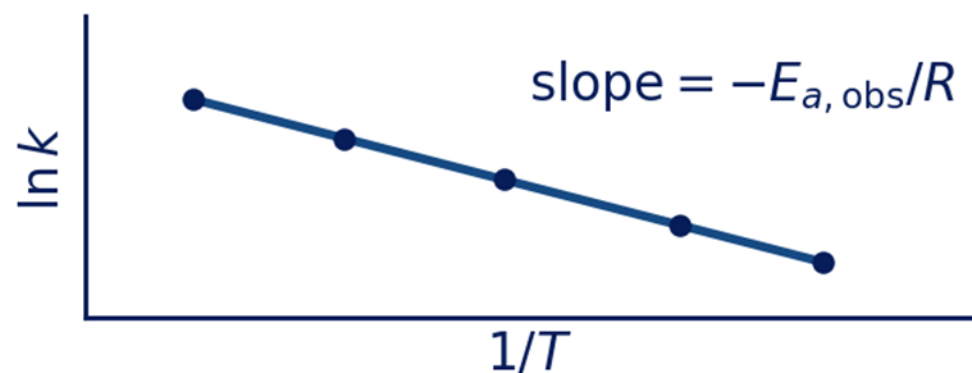


What Does Activation Energy Actually Represent?

Measured temperature dependence and molecular reaction pathways are related – but not identical.

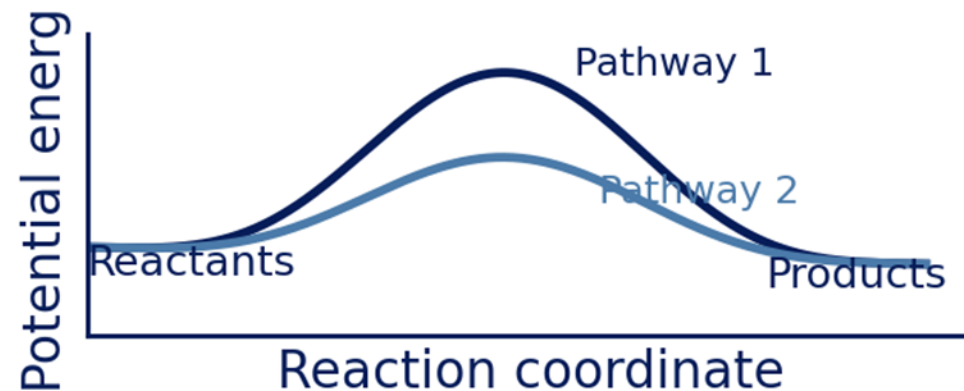
What experiments tell us

- Measure rate constants at several temperatures
- Arrhenius gradient gives the fitted activation energy
- It describes the observed process under tested conditions



What molecular pathways tell us

- Elementary steps have pathway-specific energy barriers
- Several steps may contribute to one measured rate
- The fitted value may be an apparent activation energy



Key distinction Experimental E_a characterises a measured kinetic process – not automatically a single molecular barrier.

Assigning a pathway requires independent evidence; E_a alone does not establish stability or initiation sensitivity.

How Do We Determine Rate Constants at Different Temperatures?

1

Select several temperatures

Carry out experiments at a range of well-controlled temperatures, keeping all other conditions the same (e.g. concentration, solvent, pH, sample form).

2

Measure reaction progress

Monitor the change in concentration (or another suitable observable) as a function of time at each temperature.

3

Determine the rate constant, k

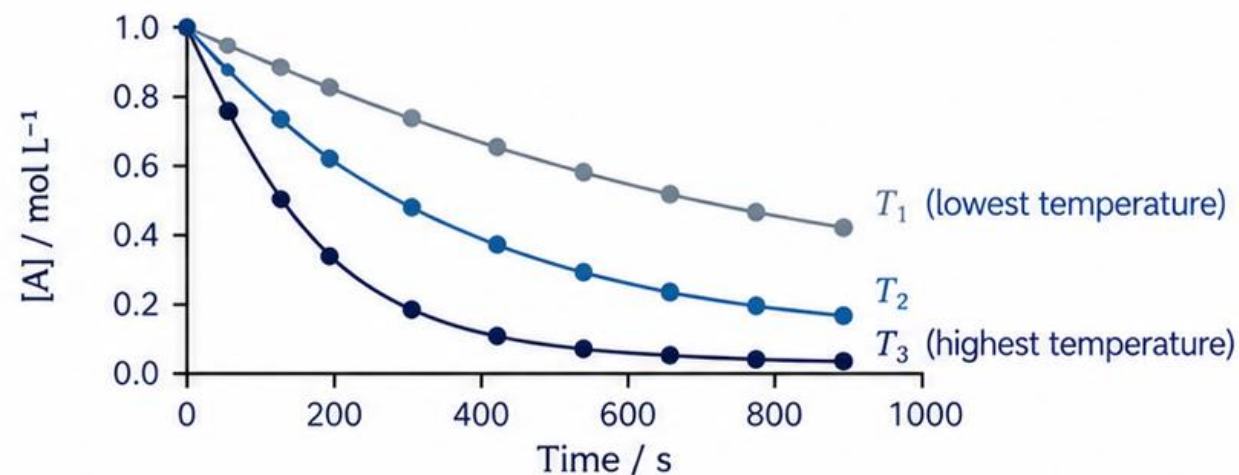
Fit the appropriate kinetic model to the data at each temperature (e.g. first-order, second-order) to obtain a value of k .

4

Compare k across temperatures

Use the resulting $k(T)$ values to investigate the temperature dependence using the Arrhenius equation.

Illustrative concentration–time data



Illustrative rate constants

Temperature, T / K	Rate constant, k / s^{-1}
293	0.002
303	0.004
313	0.008

Arrhenius analysis begins with experimentally determined rate constants at known temperatures.

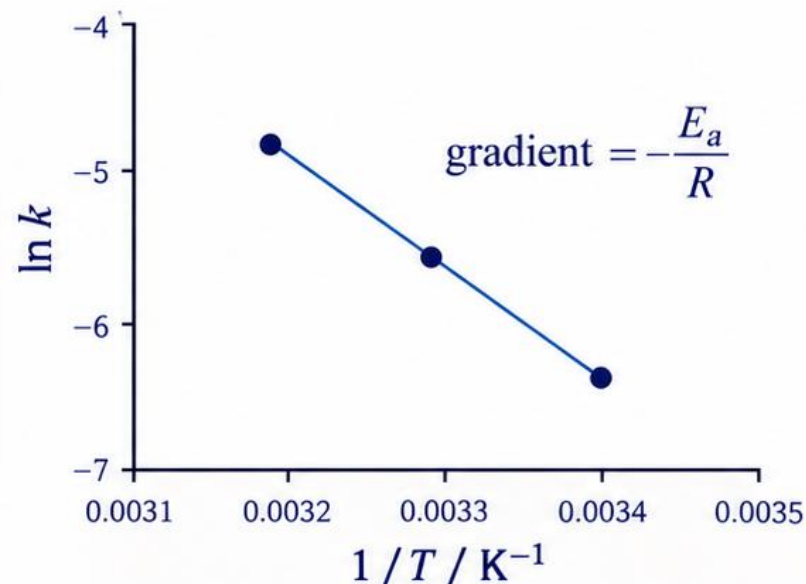


Constructing and Interpreting an Arrhenius Plot

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

Experimental data

T / K	k / s^{-1}	$1/T / \text{K}^{-1}$	$\ln k$
293	0.0020	0.003413	-6.215
303	0.0040	0.003300	-5.521
313	0.0080	0.003195	-4.828



Kinetic parameters from the Arrhenius plot

Gradient = -6355 K

$$E_a = -(\text{gradient})R = 52.8 \text{ kJ mol}^{-1}$$

Intercept = $\ln A$

$$A = e^{\text{intercept}} = 5.2 \times 10^6 \text{ s}^{-1}$$

The intercept is obtained by extrapolating the fitted line to $1/T = 0$.

A straight line on the Arrhenius plot gives the activation energy, E_a , from the gradient and the pre-exponential factor, A , from the intercept.

How Much Does the Rate Constant Change with Temperature?

The Arrhenius equation can be rearranged to compare rate constants at two temperatures:

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

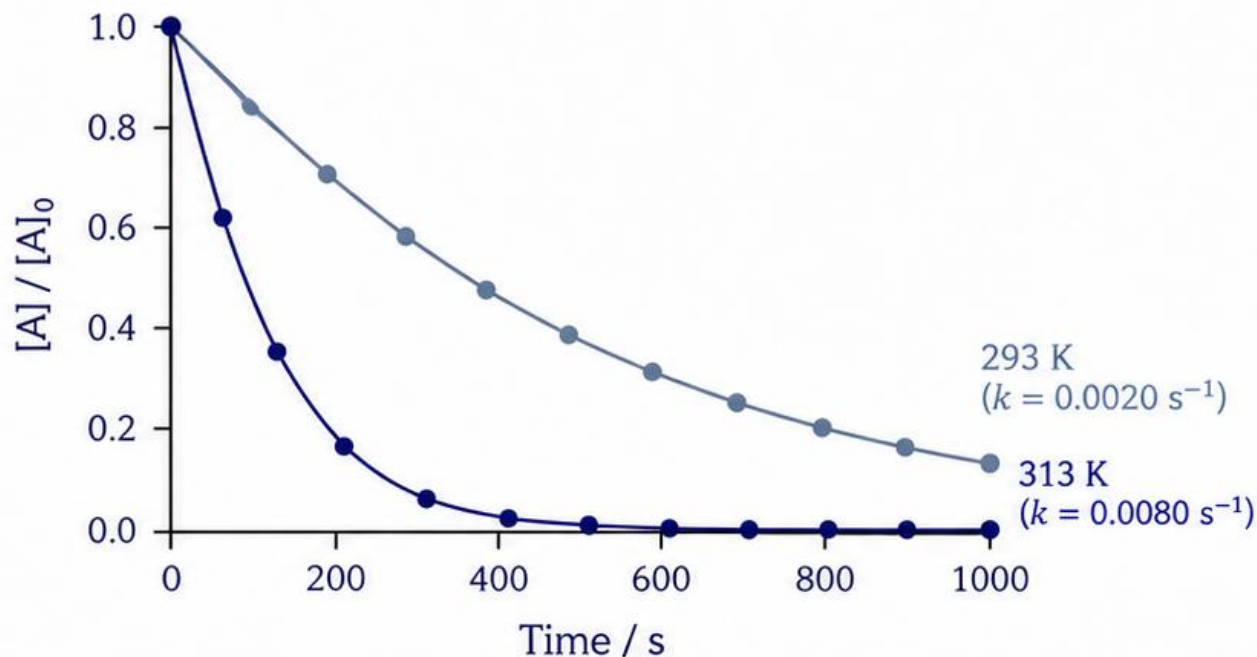
Example: predict k at 313 K

From the Arrhenius plot (previous slide), $E_a \approx 53 \text{ kJ mol}^{-1}$.
Given $k_1 = 0.0020 \text{ s}^{-1}$ at $T_1 = 293 \text{ K}$, predict k_2 at $T_2 = 313 \text{ K}$:

$$\ln \left(\frac{k_2}{0.0020} \right) = \frac{53000}{8.314} \left(\frac{1}{293} - \frac{1}{313} \right) \approx 1.39$$

$$\frac{k_2}{0.0020} \approx 4.0 \quad \rightarrow \quad k_2 \approx \mathbf{0.0080 \text{ s}^{-1}}$$

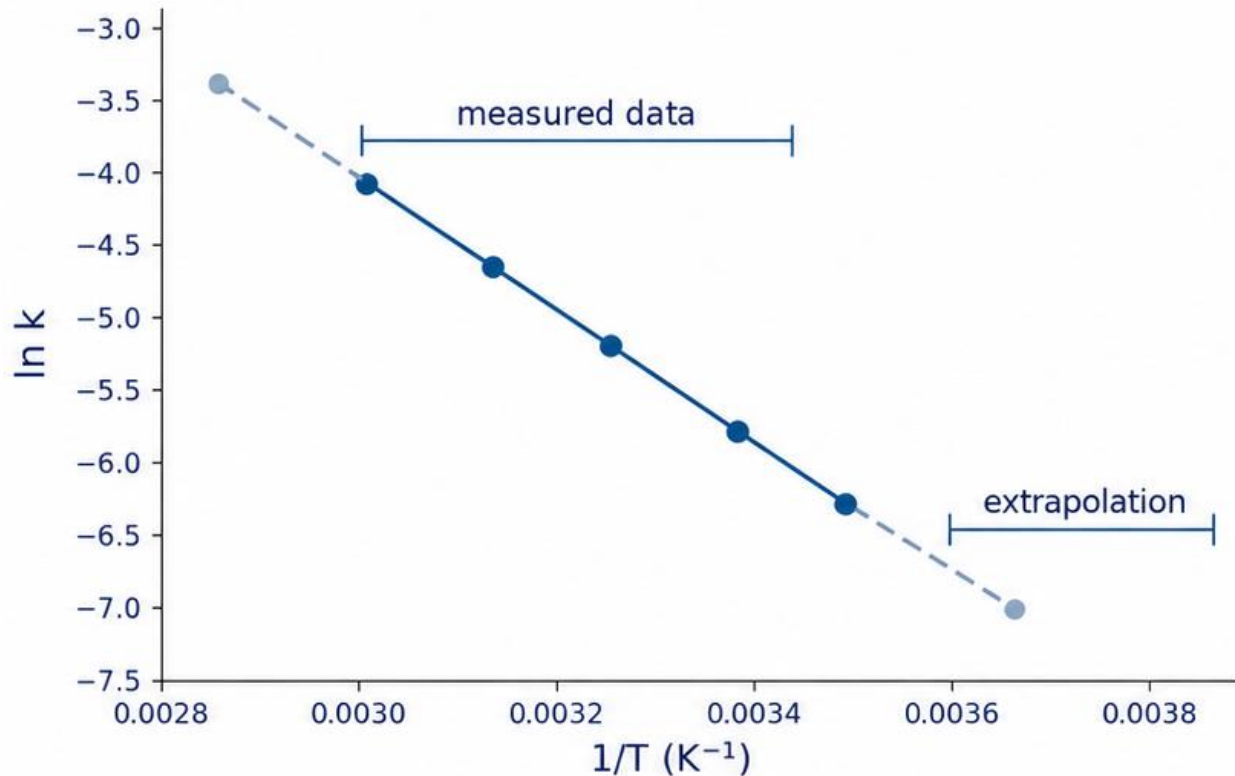
Illustrative first-order concentration–time profiles



For this example, a 20 K increase (293 → 313 K) leads to an approximately fourfold increase in the rate constant and much faster concentration decay.



Can We Predict Reaction Rates Beyond the Measured Temperature Range?



Lower temperatures lie to the right on an Arrhenius plot.

1. Interpolation and extrapolation

- Interpolation uses the fitted relationship within the measured temperature range.
- Extrapolation predicts behaviour outside the measured range.

2. Extrapolation requires assumptions

- The same kinetic model remains valid.
- No important phase change occurs.
- No new dominant pathway becomes important.

3. Why this matters in OME

- Accelerated ageing often uses elevated-temperature data.
- Good high-temperature fits do not automatically guarantee accurate long-term storage predictions.

Question: What assumptions are we making when we use high-temperature data to predict behaviour at lower storage temperatures?

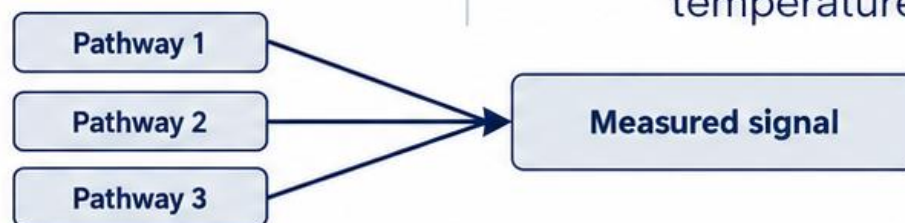
What Is an Apparent Activation Energy?

Simple kinetic process

- One kinetic relationship describes the measured behaviour.
- Arrhenius analysis gives an activation energy associated with the specified process.
- One model may describe the measured temperature range well.

Complex decomposition process

- Several reactions or physical processes may contribute to the measurement.
- Arrhenius fitting may produce an apparent activation energy representing combined observed behaviour.
- The apparent activation energy may change with temperature, conversion or dominant pathway.



Several pathways can contribute to one experimental signal.

An apparent activation energy describes the temperature dependence of measured kinetic behaviour; it does not necessarily identify the barrier of an individual elementary reaction.

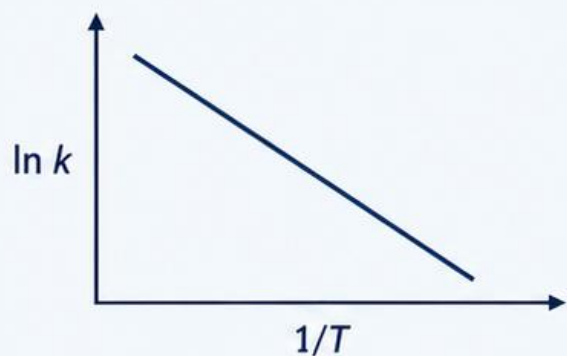
Apparent does not mean incorrect — it means model- and condition-dependent.

When Does Arrhenius Behaviour Become More Complex?

A single Arrhenius model predicts a straight line on a plot of $\ln k$ against $1/T$, provided A and E_a remain constant.

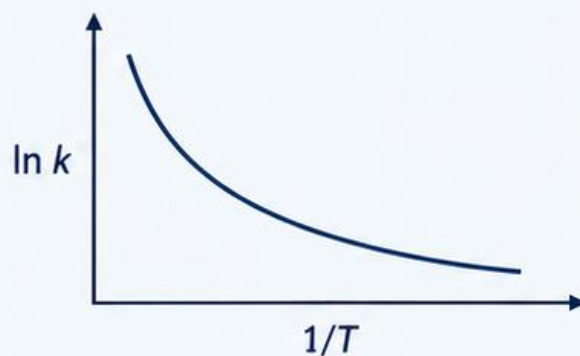
What does the experimental evidence look like?

Single Arrhenius relationship



Approximately constant gradient
→ one fitted E_a

Non-Arrhenius behaviour



Changing gradient
→ temperature dependence varies

Schematic examples. Curvature or a change in gradient should prompt further investigation; it does not identify a mechanism by itself.

Why might the relationship change?

Changing reaction pathways

Different decomposition reactions may dominate at different temperatures.

Phase or structural changes

Melting, solid-state transitions or structural changes may alter the observed kinetics.

Transport and experimental effects

Diffusion, heat transfer or thermal lag may influence the measured temperature dependence.

A straight-line Arrhenius fit may be valid over a limited temperature range, but its parameters should not automatically be applied beyond that range.

Evaluating Arrhenius Predictions for Energetic Materials

Case study – accelerated ageing of a propellant

Researchers investigate chemical ageing by measuring stabiliser depletion in a solid propellant at elevated temperatures.

Experimental evidence	Observation
HPLC measurements	Stabiliser concentration decreases during ageing at 60, 70 and 80 °C.
Kinetic analysis	First-order models describe the measured stabiliser depletion reasonably well.
Arrhenius analysis	An approximately linear relationship is obtained over the tested temperatures.
Storage conditions	The material is intended to be stored near 25 °C.



Questions for discussion



The researchers use their Arrhenius model to extrapolate the stabiliser-depletion rate to 25 °C and make the following claim:

“Our results demonstrate that the propellant will remain safe for 10 years at 25 °C.”

- 1 What does the experimental evidence actually demonstrate?**
Consider what has been measured and over which temperature range.
- 2 What assumptions are required to extrapolate the results to 25 °C?**
What must remain unchanged for this prediction to be valid?
- 3 Is the 10-year safety claim justified?**
What additional evidence would be needed before a reliable conclusion about storage lifetime can be made?

Think critically about what the data show, what is being assumed and what further evidence is required.

This is a hypothetical teaching example – not an actual stability assessment.



Temperature Dependence – Key Takeaways

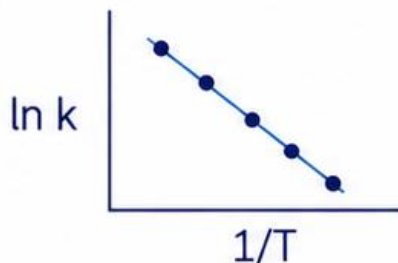
1 Measure



- Determine rate constants, k , at different temperatures.
- Keep other conditions the same.



2 Analyse



- Plot $\ln k$ against $1/T$.
- Gradient gives the activation energy, E_a .
- Intercept gives the pre-exponential factor, A .



3 Predict



- Use k , E_a and A to estimate rate constants at other temperatures.
- Interpolation is generally more reliable than extrapolation.



4 Evaluate



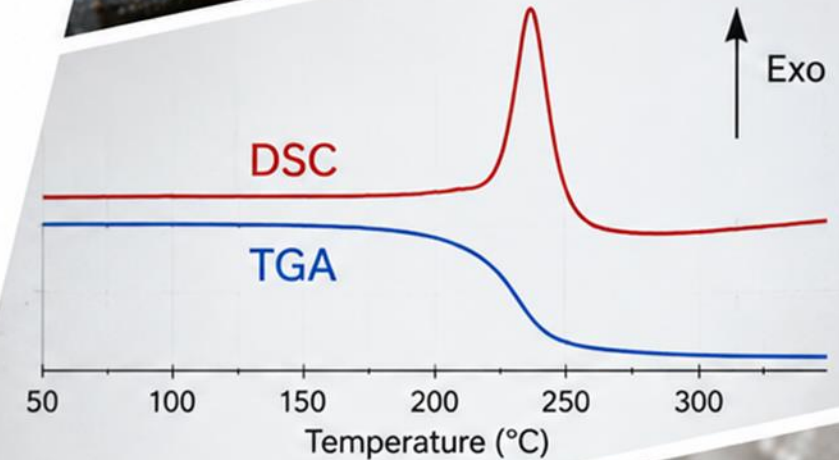
- Check the assumptions and limitations.
- The kinetic model may not remain valid.
- Changing mechanisms or material properties can lead to non-Arrhenius behaviour.

An Arrhenius model can describe and predict temperature-dependent kinetics, but its validity must be supported by experimental evidence.



Why Does Kinetics Matter During Storage?

From kinetic models to the chemistry of decomposition, thermal stability and ageing in energetic materials.



Why Is Energetic-Material Decomposition Complex?

Energetic materials rarely decompose by a single, simple reaction pathway.

1 Several chemical pathways

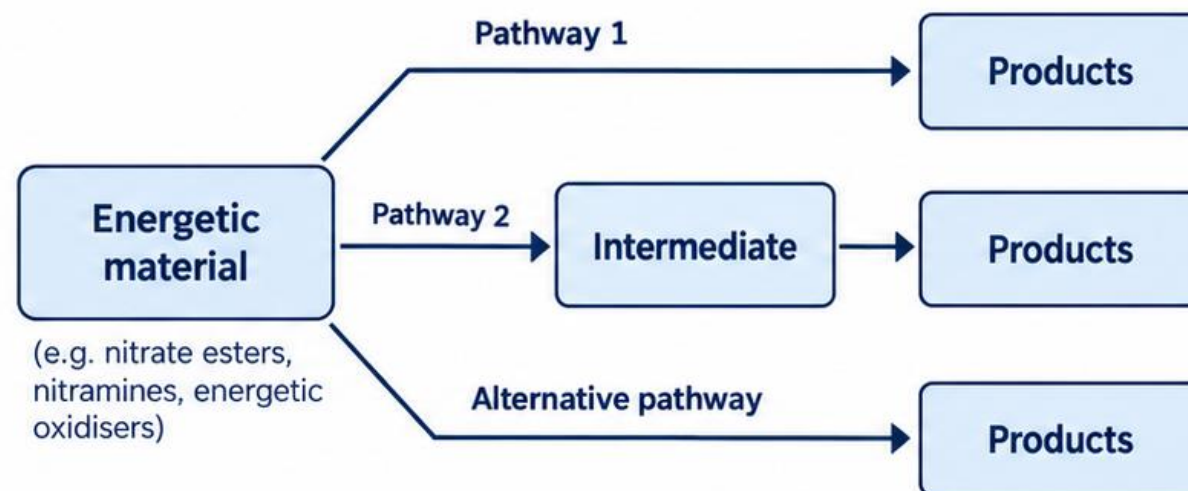
Different bonds and functional groups can react under heating, giving competing decomposition routes.

2 Intermediates and secondary reactions

Primary decomposition products may react further, so the observed behaviour reflects more than one step.

3 Changing material environment

Phase changes, gas release, impurities, confinement and the solid-state structure can all influence the measured rate.

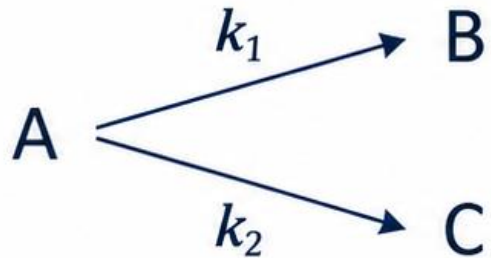


Observed decomposition kinetics often describe the combined behaviour of several chemical and physical processes.

Parallel and Consecutive Decomposition Reactions

Energetic materials may decompose through competing pathways or through sequential steps.

Parallel reactions



- One reactant can form more than one product.
- Each pathway can have different kinetics.
- Product distribution depends on the relative pathway rates.

Consecutive reactions



- An intermediate forms and then reacts further.
- The intermediate may increase and then decrease.
- Overall behaviour depends on the rates of both steps.

Observed decomposition behaviour may reflect several coupled reactions rather than one single step.

Why Can Decomposition Accelerate with Time?

1

Induction period

- Initially the reaction rate can be low.
- Reactive intermediates or products may build up before a more rapid stage begins.
- This can give an apparent delay in decomposition.

2

Autocatalytic behaviour

- Some decomposition products can promote further decomposition.
- As the concentration of these products increases, the reaction rate increases.
- Example (B is a reactive product acting as a catalyst):

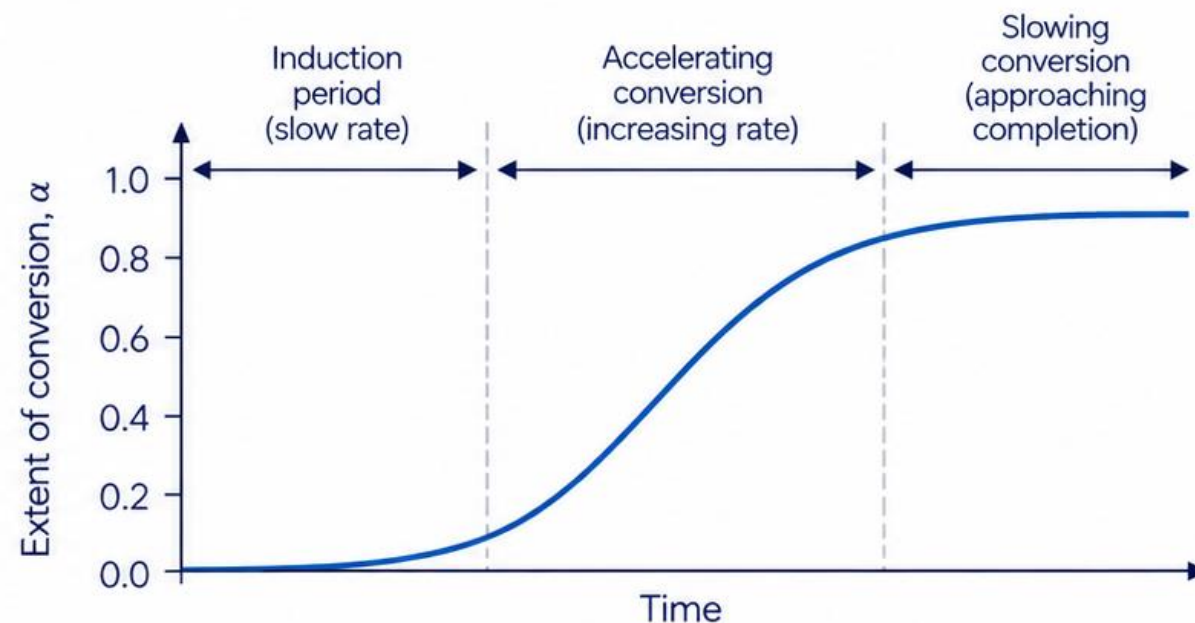


A small initial amount of B (or its formation by another reaction) is needed to start the autocatalytic process.

3

Implications for chemical stability

- The reaction rate can increase with time, even when the external temperature is constant.
- A simple first-order model may not adequately describe this behaviour.



Important points

- Autocatalytic behaviour requires an initial source of the reactive product (e.g. a small initial amount or formation by another reaction).
- A sigmoidal conversion–time curve does not uniquely prove autocatalysis; similar behaviour can also arise from nucleation and growth or other processes.
- Autocatalysis can occur without any increase in external temperature.

Decomposition rates can accelerate as reactive products accumulate, even at constant temperature.

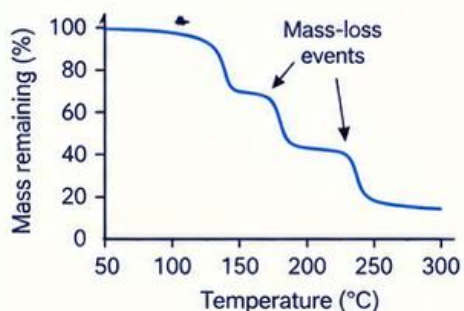
How Do We Investigate Thermal Decomposition?

A range of complementary techniques are used to measure chemical and physical changes during heating or storage.

- Different techniques provide complementary information about decomposition.
- Each technique measures a specific property of the material.
- No single technique can describe the complete decomposition chemistry.
- Combining evidence helps to identify possible reactions, intermediates and products.

TGA (thermogravimetric analysis)

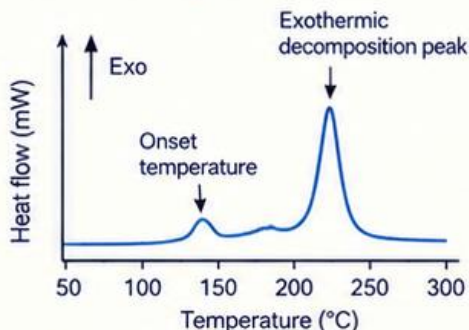
Mass change



- Measures change in sample mass with temperature or time.
- Stepwise mass loss indicates one or more mass-loss events (e.g. decomposition, desorption or volatilisation).

DSC (differential scanning calorimetry)

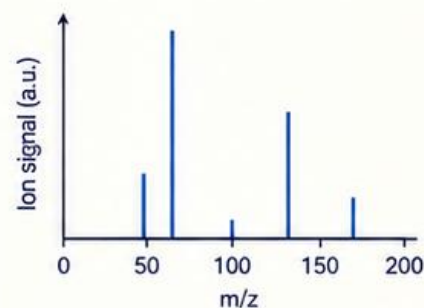
Heat-flow response



- Measures heat-flow differences associated with thermal events (e.g. phase transitions or chemical reactions).
- Peak position and shape provide information about the thermal event.
- The onset temperature depends on the heating rate and experimental conditions.

Evolved-gas analysis (e.g. MS or FTIR)

Gaseous products

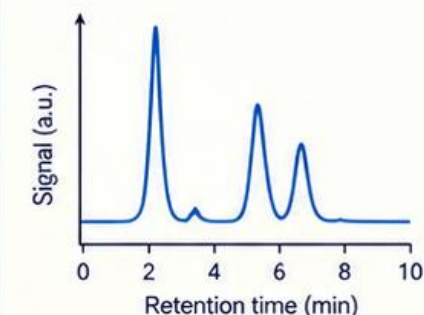


- Analyses gaseous or volatile species released during heating.
- Provides information about the identity and relative abundance of evolved gases (e.g. using mass spectrometry or FTIR).
- Quantification requires calibration and appropriate reference data.

HPLC

(high-performance liquid chromatography)

Specific chemical species



- Separates and detects specific chemical species (e.g. stabilisers, intermediates or decomposition products).
- Can be used to quantify selected compounds when a validated method is available.

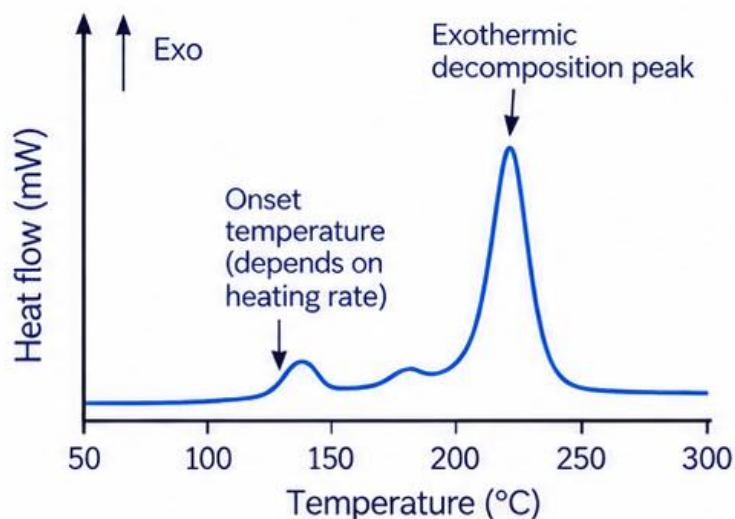
Thermal-analysis techniques provide complementary information, but none can uniquely identify the full decomposition mechanism or all products.

What Can We Actually Conclude from Thermal-Analysis Curves?

Thermal-analysis data provide valuable information, but they have limitations.

DSC (heat flow)

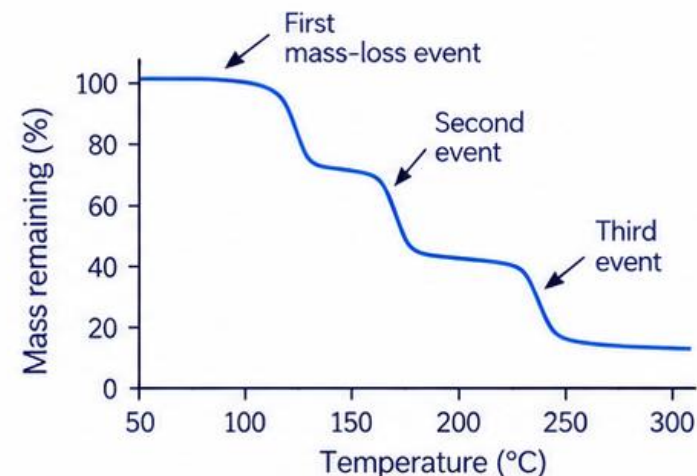
- Peaks show endothermic or exothermic events.
- The measured onset temperature indicates when a thermal event begins, but it depends on the heating rate and experimental conditions.
- Peak shape, position and size can suggest overlapping or multiple processes.
- A DSC curve does not uniquely identify the reaction or the products.



- Peak area (with calibration) can provide information about the enthalpy change.
- Multiple or overlapping peaks may indicate more than one process, but do not prove separate reactions.

TGA (mass change)

- Shows the change in sample mass with temperature or time.
- Stepwise mass loss indicates multiple mass-loss events, which may involve different processes (e.g. decomposition, desorption or volatilisation).
- The onset temperature for mass loss depends on the heating rate and experimental conditions.
- A TGA curve does not uniquely identify the reaction mechanism or specific products.



- Each mass-loss step may correspond to one or more processes.
- Some mass changes can also occur through evaporation, desorption or loss of volatile species.
- TGA does not identify the chemical identity of the products.

Thermal-analysis curves provide evidence about when and how decomposition occurs, but they do not uniquely identify reaction mechanisms or products.

How Do We Describe Decomposition Progress in a Solid?

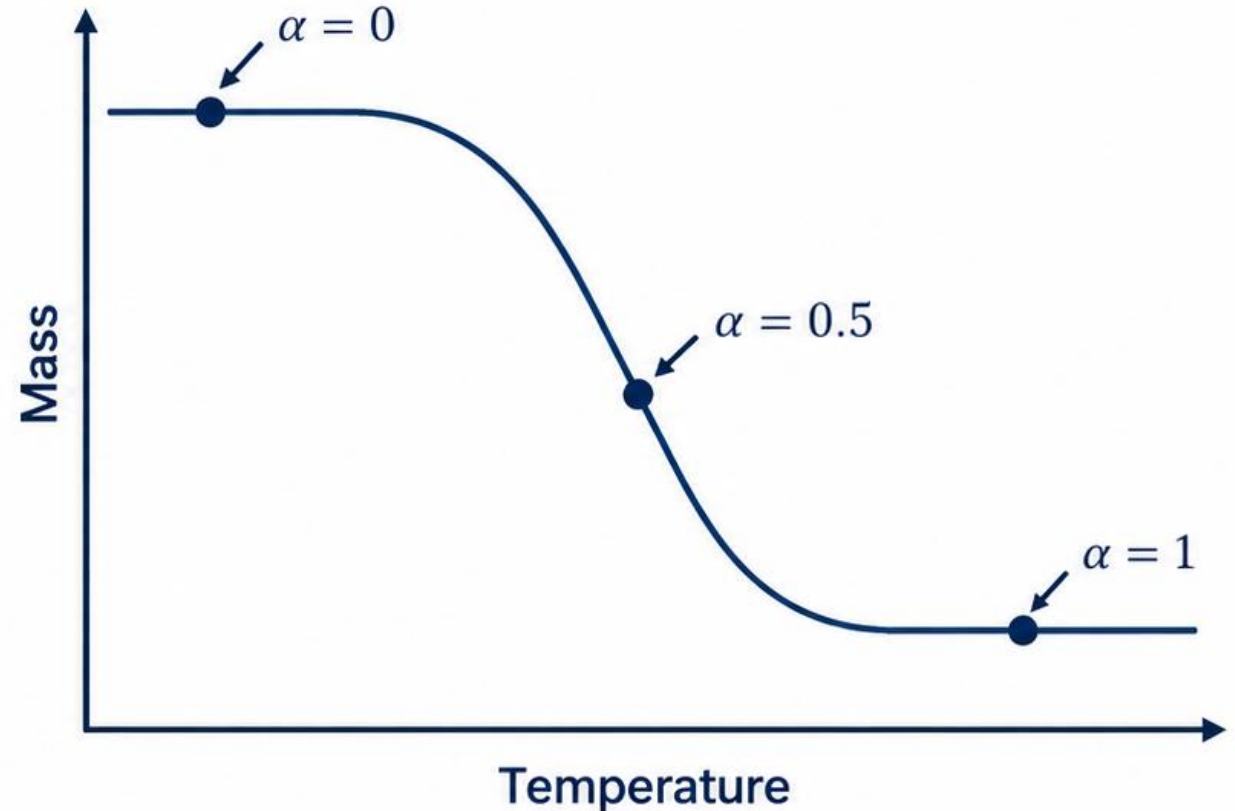
$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

For a mass-loss process:

- m_0 = initial mass
- m_t = mass at time t or temperature T
- m_f = final mass for the defined event
- $\alpha = 0$: no conversion yet
- $\alpha = 1$: defined mass-loss event complete

Important

α describes progress through a defined event. It does not necessarily equal the fraction of molecules chemically decomposed.



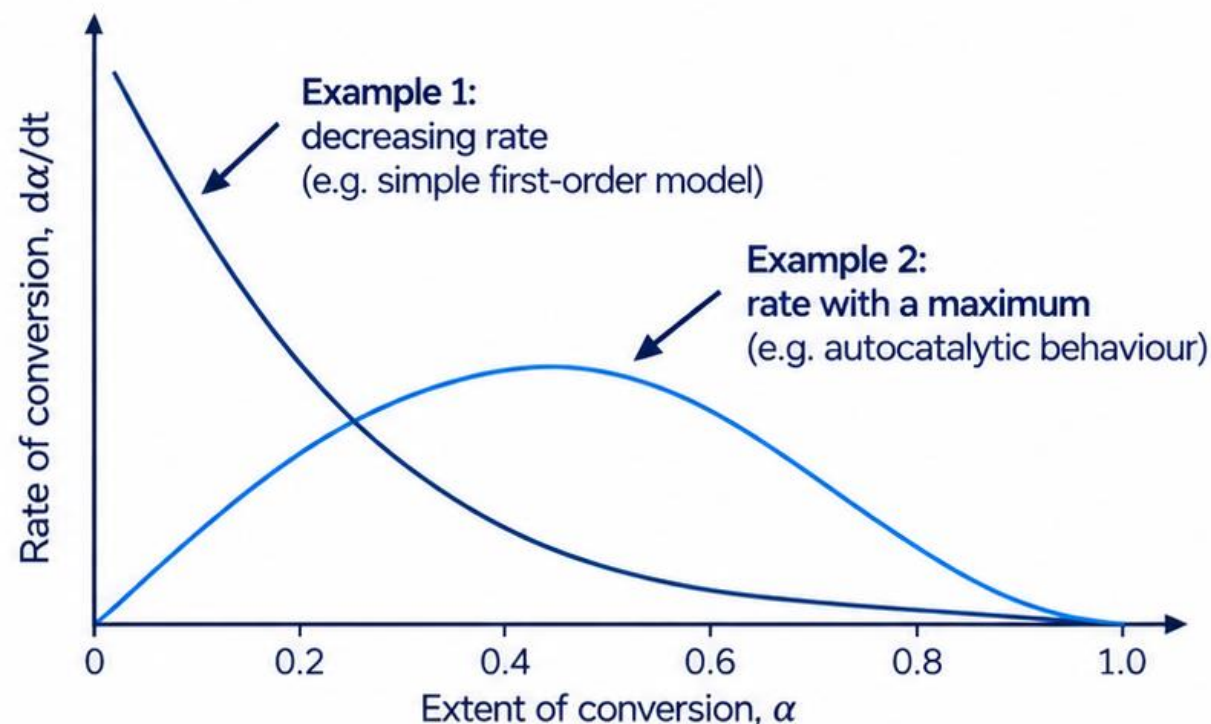
Extent of conversion, α , helps us describe how far a solid-state decomposition process has progressed.

How Does Conversion Affect Decomposition Rate?

$$\frac{d\alpha}{dt} = k(T) f(\alpha)$$

α	extent of conversion (0 to 1)
$d\alpha/dt$	rate of conversion (s^{-1})
$k(T)$	temperature-dependent rate constant (s^{-1})
$f(\alpha)$	function describing how the rate depends on conversion (e.g. decreasing, increasing or showing a maximum)

- As decomposition proceeds, reactants are consumed and products accumulate.
- Even at constant temperature, the observed rate can change with conversion, α .



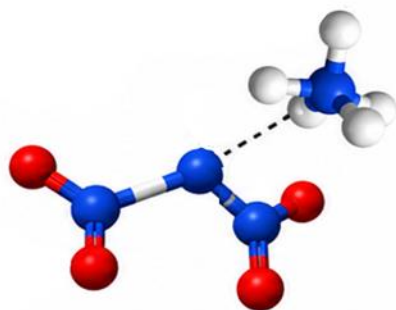
These are illustrative conversion-dependent rate functions for different kinetic models, not experimental data for a specific reaction.

The decomposition rate in a solid can depend on the extent of conversion, not just on temperature.

Case Study – Thermal Decomposition of Ammonium Dinitramide

Experimental studies show that ADN decomposes over a relatively narrow temperature range and produces multiple gaseous products, indicating complex reaction chemistry.

Ammonium dinitramide (ADN)

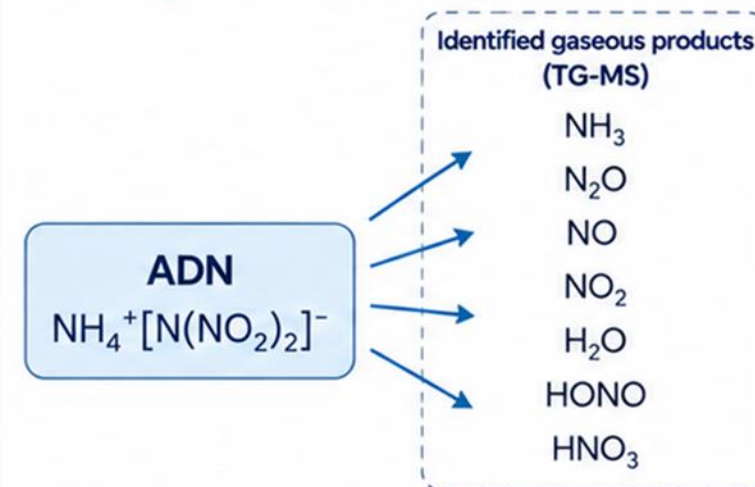


- Energetic oxidiser used in propellant formulations.
- High nitrogen content and no carbon.
- Investigated as a low-smoke alternative to ammonium perchlorate.

Published experimental findings

Measurement	Reported result (Vyazovkin and Wight, 1997)
Technique	DSC and TG-MS (heating from ~130 to 230 °C)
DSC (heat release)	Overall heat of decomposition: $240 \pm 40 \text{ kJ mol}^{-1}$
TG-MS (evolved gases)	Gaseous products identified: NH_3 , N_2O , NO , NO_2 , H_2O , HONO and HNO_3
Conclusion (from authors)	Evidence for complex, multi-step decomposition involving intermediates and competing reaction pathways.

Decomposition products



Multiple products suggest complex reaction chemistry and possible secondary reactions.

Based on Vyazovkin and Wight, J. Phys. Chem. A, 1997, 101, 5653–5658.

ADN thermal decomposition produces multiple gaseous species, providing experimental evidence of complex reaction chemistry.

What Does the ADN Evidence Tell Us About Decomposition Kinetics?

Early decomposition

$$E_{a,\text{app}} = 175 \pm 20 \text{ kJ mol}^{-1}$$

As conversion
progresses



Near completion

$$E_{a,\text{app}} = 125 \pm 20 \text{ kJ mol}^{-1}$$

From Vyazovkin and Wight (1997), *Journal of Physical Chemistry A*, 101, 5653–5658.
DOI: 10.1021/jp962547z.

Extent of conversion, α

0



1

Key interpretations

- Apparent activation energy changes with reaction progress.
- Carrier-gas flow experiments suggest that evolved products affect the rate.
- Multiple pathways were proposed; kinetic measurements alone do not prove the mechanism.

Changing $E_{a,\text{app}}$ is evidence that a single constant-activation-energy model may be inadequate.

How Do Stabilisers Influence Chemical Ageing?

Stabilisers such as diphenylamine (DPA) react with reactive nitrogen-containing species formed during nitrocellulose ageing.

1

Nitrocellulose ageing can generate reactive nitrogen-containing species

- Nitrocellulose contains nitrate ester groups ($-O-NO_2$) on the cellulose backbone.
- Thermal or chemical degradation can release reactive species such as NO_2 and $HONO$.
- These species can initiate further reactions and contribute to autocatalytic decomposition.

2

Diphenylamine reacts with degradation species

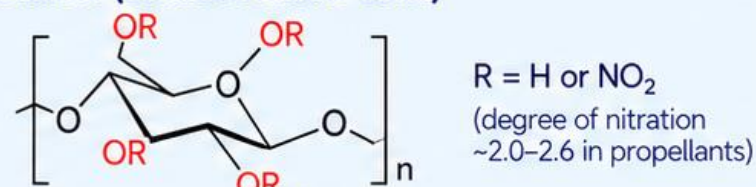
- DPA acts as a stabiliser by reacting with reactive nitrogen-containing species (e.g. NO_2 , $HONO$).
- This reduces their concentration and can slow further decomposition.

3

DPA is converted into reaction products

- Reaction with nitrogen oxides forms several products, including nitroso- and nitratediphenylamines.
- Some derivatives may retain stabilising activity, although generally less effective than the parent DPA.

Nitrocellulose (cellulose nitrate ester)



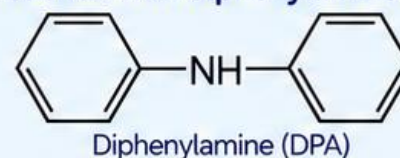
- Cellulose polymer with nitrate ester groups ($-O-NO_2$).
- Ageing can release reactive nitrogen-containing species.

Reactive nitrogen-containing species

e.g. NO_2 , $HONO$, HNO_3 , NO , N_2O

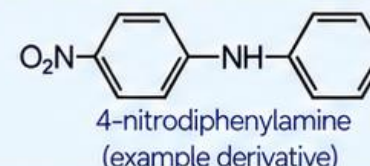
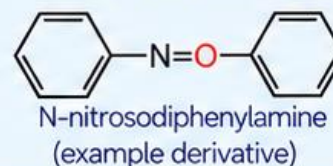
- Formed during degradation of nitrocellulose.
- Can react further and promote additional decomposition.

Reaction with diphenylamine (DPA)



- DPA reacts with reactive nitrogen-containing species (e.g. NO_2 , $HONO$).
- This reduces their concentration in the formulation.

Example DPA reaction products (not exhaustive)



- Several derivatives can form (e.g. nitroso- and nitrated products).
- Some derivatives may retain stabilising activity.

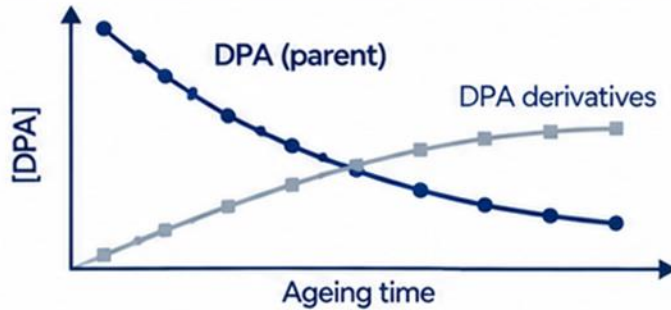
Stabiliser depletion and the formation of stabiliser derivatives indicate chemical changes in the propellant, but they do not, on their own, establish its overall stability.



What Experimental Evidence Reveals Propellant Ageing?

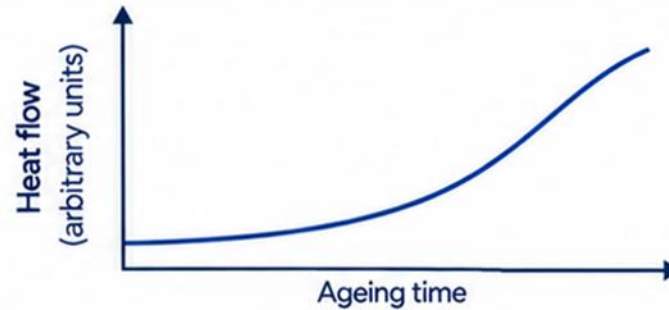
Different analytical techniques provide complementary evidence of chemical changes during storage.

HPLC – stabiliser composition



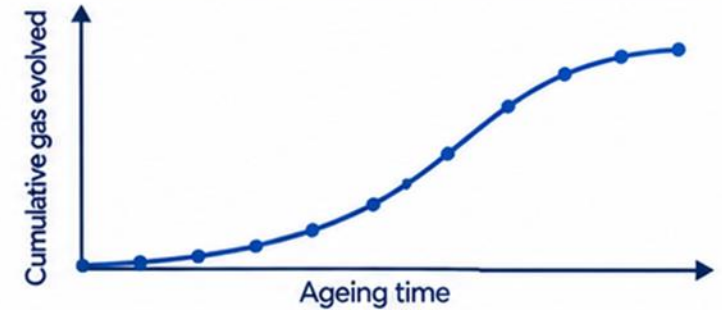
- Measures the concentration of DPA and selected reaction products.
- Shows consumption of the original stabiliser and formation of derivatives.
- Some derivatives may retain stabilising activity.

Heat-flow calorimetry



- Measures heat released during controlled ageing.
- Evidence of ongoing exothermic chemical activity.
- Does not identify specific chemical reactions or products.

Gas evolution analysis



- Measures the total amount of gas evolved (and, where used, the composition).
- Evidence of gaseous degradation products (e.g. NO_x , HNO_x , H_2O).
- Supports the presence of decomposition reactions during storage.



Question

A propellant sample contains less DPA after accelerated ageing, but its measured heat flow remains low. Are these results contradictory?

Key point

Not necessarily. The measurements investigate different aspects of ageing and must be interpreted together.

**Complementary measurements reveal different aspects of chemical ageing;
no single signal provides a complete assessment of propellant stability.**

What Changes in Modern Heterogeneous OME Formulations?

Component interactions

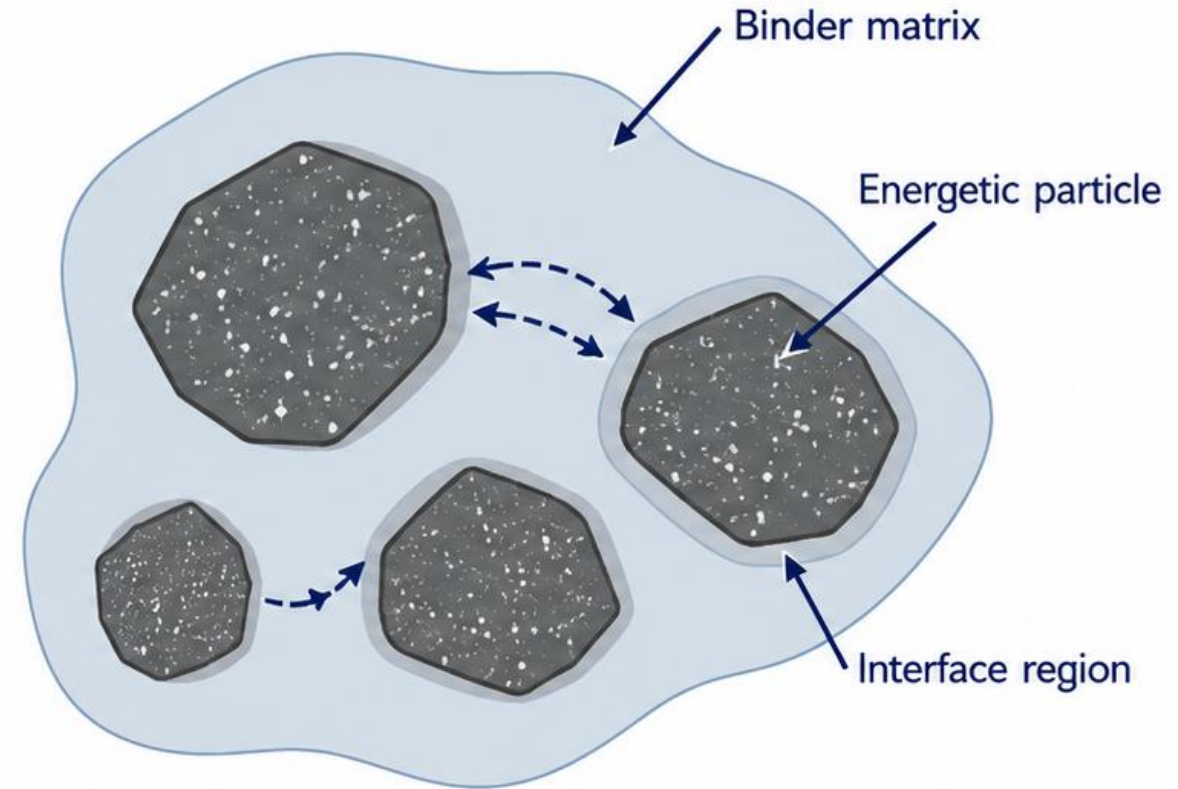
Decomposition products from one component may react with another and alter degradation pathways.

Interfaces and transport

Migration and interfacial reactions can influence observed ageing behaviour.

Ageing changes

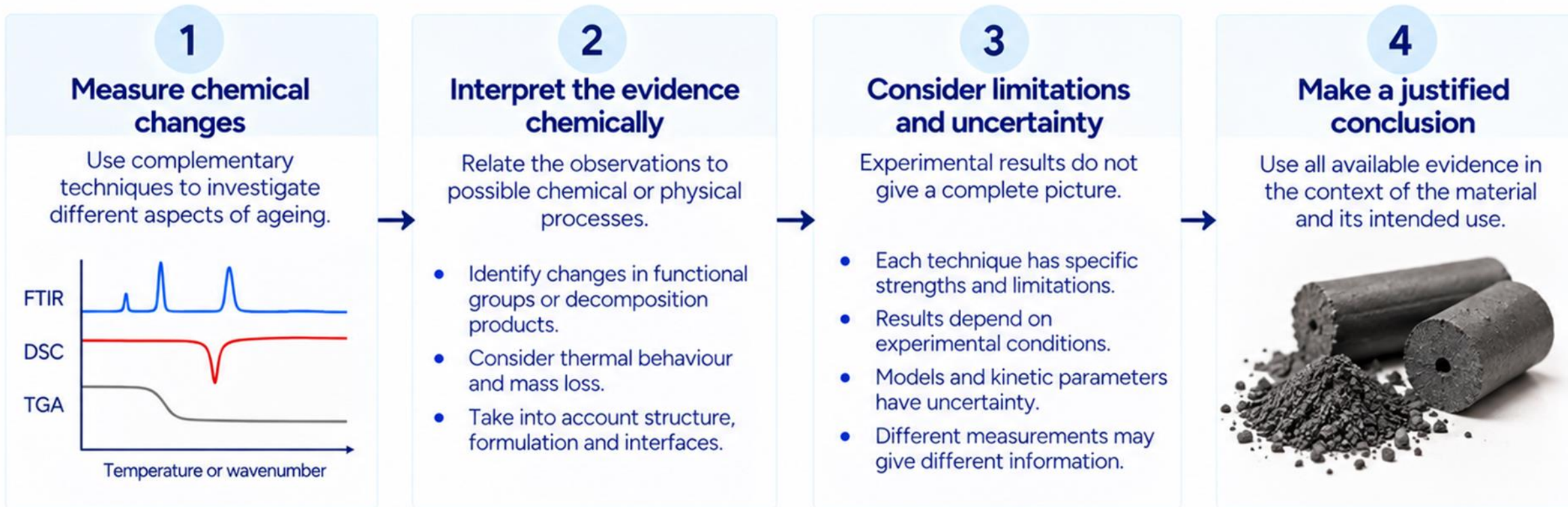
Binder degradation, additive migration and structural change may affect stability and decomposition behaviour.



The chemical stability of a multicomponent energetic formulation depends on interactions between its constituents, not only on their individual properties.

How Can We Evaluate Chemical Stability?

A reliable assessment requires complementary evidence and critical interpretation.



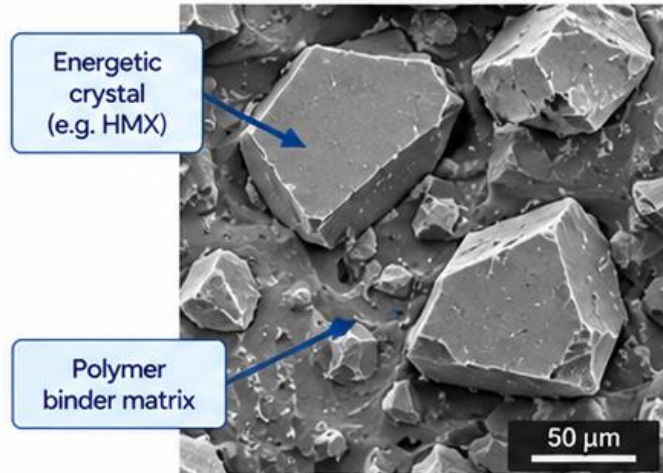
Key takeaway: A defensible assessment of chemical stability requires multiple, consistent lines of evidence and an understanding of their limitations.

What Can We Conclude from Experimental Stability Evidence?

Consider the following results for a polymer-bonded explosive (PBX) after a period of controlled storage.

Case study – ageing of a polymer-bonded explosive

A PBX formulation containing energetic crystals in a polymer binder is analysed before and after a period of accelerated storage.



Example microstructure of a PBX formulation (SEM image, representative).

Technique	Observation after ageing (compared with unaged sample)
FTIR	- A change in an absorption band associated with the polymer binder is observed. - No significant change in the main energetic-crystal bands.
DSC	- The main exothermic event occurs at a slightly lower temperature compared with the unaged sample. - The shape of the event is similar.
TGA	- The overall mass-loss profile is approximately unchanged. - No additional low-temperature mass loss is observed.

Researcher's conclusion:

"The material has not undergone significant ageing because its TGA behaviour is unchanged."

Hypothetical teaching example. These are illustrative observations, not published experimental results.

Questions for discussion

1

Evidence

What does each experimental observation actually demonstrate? Be specific about what information each technique provides.

2

Interpretation

Is the researcher's conclusion justified based on these results? Explain your reasoning.

3

Further investigation

What additional information would you require before making a chemical stability assessment for this PBX formulation?

**Different measurements may reveal different aspects of ageing;
a defensible chemical stability assessment requires their combined interpretation.**

Practical 2 – How Can We Determine a Rate Law Experimentally?

The iodine clock reaction (LR2) is used to investigate the dependence of reaction rate on reactant concentration.

1

Vary reactant concentrations

Change the concentration of H_2O_2 or I^- while keeping the other conditions constant (e.g. temperature, total volume).

2

Measure the clock time

Mix the solutions and record the time until the permanent blue colour appears (starch-iodine complex).

3

Determine the experimental rate law

Use $1/t$ as a relative rate measure and determine the reaction orders from the experimental data.



Colour change during the iodine clock reaction (appearance of the starch-iodine complex, indicative of iodine formation).

Key reaction (overall)



Vitamin C (ascorbic acid) initially reduces the iodine formed, delaying the appearance of the blue starch-iodine colour until it is consumed.

Experimental rate law (from clock time)

$$\frac{1}{t} = k' [\text{H}_2\text{O}_2]^m [\text{I}^-]^n$$

$1/t$ is proportional to the reaction rate under the clock conditions.
 k' is an empirical constant, not necessarily the true rate constant k .

Experimental kinetic parameters are obtained from measured behaviour — not simply from the balanced chemical equation.

Session 3 – Key Chemical Conclusions

Understanding and predicting the chemical stability of OME requires chemical knowledge, experimental evidence and critical interpretation under defined conditions.

1

Molecular structure and chemical reactivity

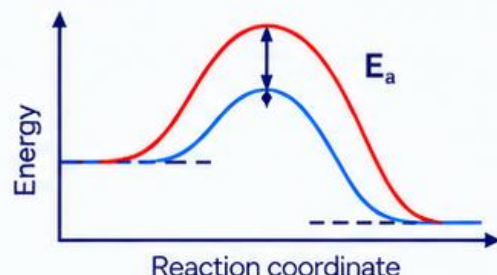
Energetic functional groups and decomposition pathways influence chemical ageing.

- Energetic groups (e.g. $-\text{NO}_2$, $-\text{ONO}_2$, $-\text{NNO}_2$) influence bond strengths and decomposition pathways.
- Decomposition can produce reactive species that may promote further reactions (e.g. autocatalysis).
- Stabilisers can react with degradation products, reducing their concentration and slowing further decomposition.

2

Reaction kinetics and temperature control rates

Reaction rates depend on temperature, extent of conversion and reaction mechanism.

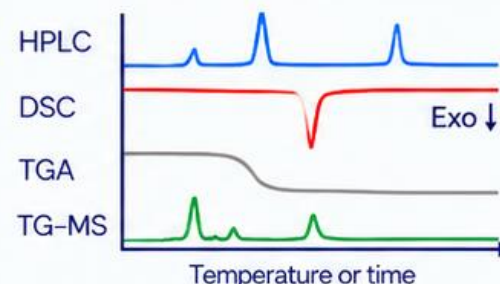


- Rates generally increase with temperature (Arrhenius behaviour).
- The rate can change as the reaction progresses (e.g. decreasing or showing a maximum).
- Predictions require appropriate kinetic models and should be treated with caution.

3

Experimental techniques provide complementary evidence

Different analytical techniques investigate different aspects of decomposition and ageing.

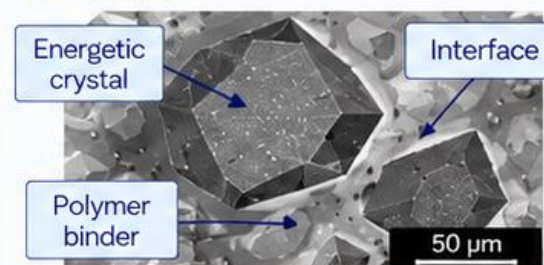


- **HPLC:** composition (e.g. stabiliser depletion and degradation products).
- **DSC:** heat-flow response (thermal events, exothermic decomposition).
- **TGA:** mass changes (decomposition, evaporation, volatile products).
- **TG-MS/FTIR:** evolved gases (e.g. NO_2 , HONO , HNO_3 , NO , N_2O). A complete assessment requires combined interpretation.

4

Formulation and environment affect stability

The chemical stability of a formulation depends on interactions between components and the surrounding conditions.



- Degradation products can react across interfaces and with other components.
- Interfaces and transport processes are chemically significant.
- Stability also depends on storage conditions (e.g. temperature, humidity, mechanical stress).

Key takeaway: Chemical stability in OME is a complex, multi-scale issue.

A robust assessment requires multiple, consistent lines of evidence and an understanding of their limitations.



Activity: Build your kinetics argument

Use today's chemistry to develop your own argument for the final group presentation.

Draw on reaction kinetics, temperature and stability to evaluate the performance, safety and lifetime of your chosen material.

Modern Pyrotechnics

How do reaction rates and thermal stability influence the performance and safety of modern pyrotechnic compositions?



Consider decomposition and ignition behaviour of oxidisers, fuels and metal additives, and the effect of formulation and particle characteristics.

Green Propellants

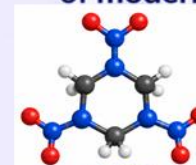
How do reaction kinetics and thermal stability affect the performance, safety and storage of reduced-toxicity propellants?



Consider alternative oxidisers (e.g. nitrates, dinitramides), fuels and binders, and how formulation influences decomposition rates, stability and gas generation.

Modern Explosive Materials

How do reaction kinetics and thermal stability affect the safety, performance and lifetime of modern explosive materials?



RDX



FOX-7

Consider how molecular structure, crystal form and formulation influence decomposition kinetics, sensitivity and long-term stability.

1. Chemical change or kinetic behaviour

(reaction/decomposition/ageing)



2. Evidence from kinetics and thermal stability

(rate, temperature, mechanism, conversion, formulation, etc.)



3. Application consequence or trade-off

(performance, safety, environment, lifetime)



4. Evidence-based conclusion

(what your analysis suggests and what remains uncertain)

Your individual task (20 minutes)

- 1 Choose **one** of the three material areas above (A, B or C).
- 2 Use today's chemistry to analyse the question for your chosen area.
- 3 Make notes using the sequence shown (1 → 2 → 3 → 4).
- 4 Identify key kinetic evidence, what it shows, and any limitations or uncertainties.
- 5 Prepare a brief, structured set of notes to support your final group presentation.



Time: 20 minutes (individual work)

- Work on your own.
- Use lecture notes, workshop activities and any other resources.
- Focus on making clear, structured notes (not a full presentation).



Keep your notes

You will use them later to support the final group work and final presentation activity.

Make sure to bring your notes with you.