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Reactivity 2.2 HL

Reaction mechanisms

Reaction mechanisms

Chemical reactions can occur in a series of steps called elementary steps; the sequence of elementary steps is the reaction mechanism.

$$2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}$$

Step 1: $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{(g)}$ slow

Step 2: $NO_2Cl_{(g)} + Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$ fast

The slowest step in the mechanism is the rate-determining step (the overall rate of reaction depends on this step).

Reaction mechanisms

$$2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}$$

Step 1: $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + \cancel{Cl_{(g)}}$ slow

Step 2: $NO_2Cl_{(g)} + \cancel{Cl_{(g)}} \rightarrow NO_{2(g)} + Cl_{2(g)}$ fast

$Cl_{(g)}$ is a reaction intermediate; it is produced in one step and consumed in the next step.

The elementary steps add up to the overall equation.

Reaction mechanisms

Consider the overall reaction shown and the proposed two-step mechanism.

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

Step 1: $NO_{2(g)} + \cancel{NO_{2(g)}} \rightarrow NO_{(g)} + \cancel{NO_{3(g)}}$ slow

Step 2: $\cancel{NO_{3(g)}} + CO_{(g)} \rightarrow \cancel{NO_{2(g)}} + CO_{2(g)}$ fast

The elementary steps add up to the overall equation.

Reaction mechanisms

When considering a proposed reaction mechanism, the following criteria are applied:

- The sum of the elementary steps must add up to the overall equation.
- The rate expression of the rate-determining step must agree with the experimentally determined rate expression.

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Catalysts and intermediates

Catalysts and intermediates

Catalysts appear in the rate-determining step (the slowest step in the mechanism).

Catalysts are not consumed in a reaction, so they appear in the reactants side of the rate-determining step and the products side of a later step.

Catalysts do not appear in the overall equation for the reaction (nor do intermediates).

Catalysts and intermediates

Step 1: $Cl\cdot_{(g)} + O_{3(g)} \rightarrow ClO\cdot_{(g)} + O_{2(g)}$ slow

Step 2: $O\cdot_{(g)} + ClO\cdot_{(g)} \rightarrow Cl\cdot_{(g)} + O_{2(g)}$ fast

Intermediate: $ClO\cdot_{(g)}$

Catalyst: $Cl\cdot_{(g)}$

Overall equation: $O_{3(g)} + O\cdot_{(g)} \rightarrow 2O_{2(g)}$

Catalysts and intermediates

Step 1: $H_2O_{2(l)} + I^-_{(aq)} \rightarrow H_2O_{(l)} + IO^-_{(aq)}$ slow

Step 2: $H_2O_{2(l)} + IO^-_{(aq)} \rightarrow H_2O_{(l)} + O_{2(g)} + I^-_{(aq)}$ fast

Intermediate: $IO^-_{(aq)}$

Catalyst: $I^-_{(aq)}$

Overall equation: $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

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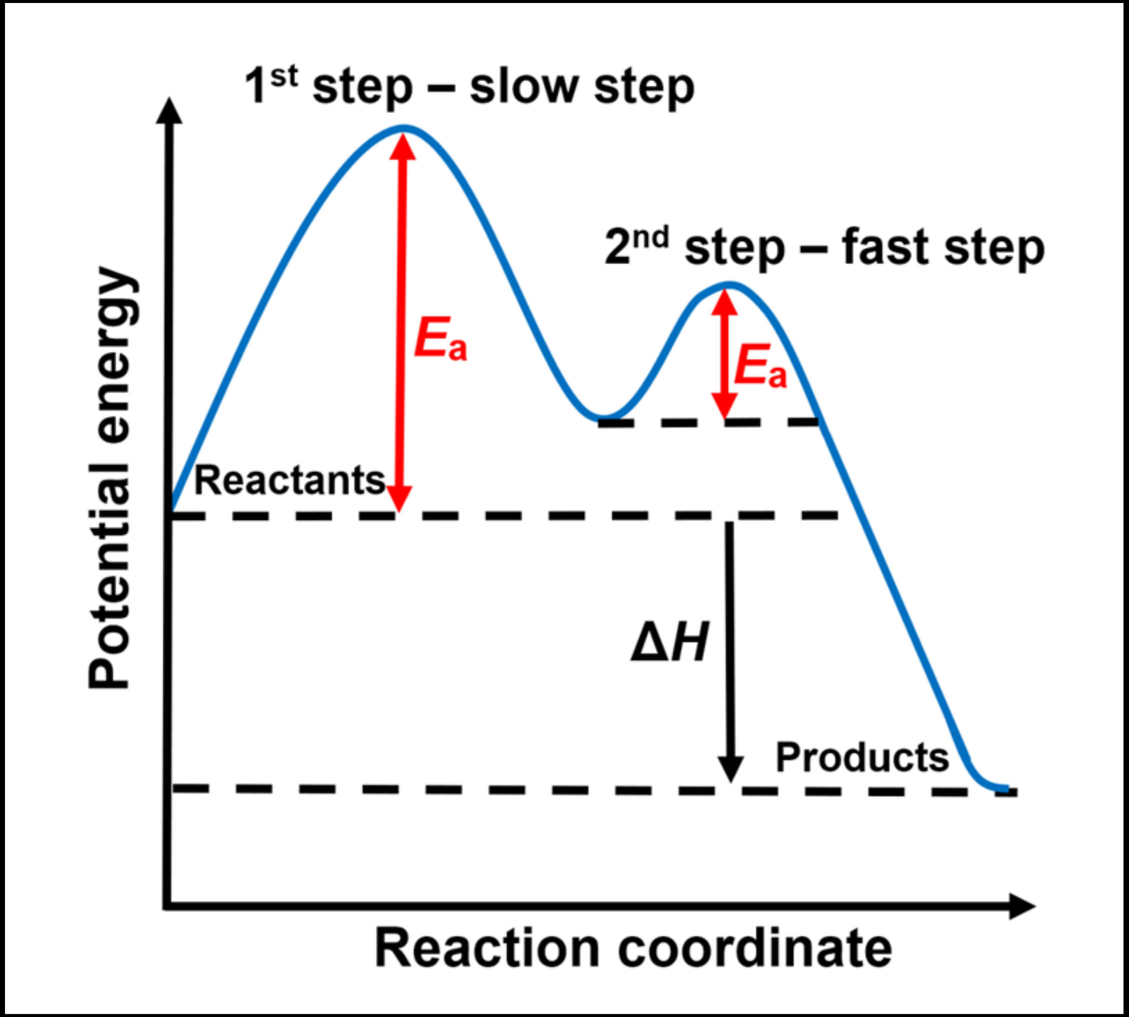
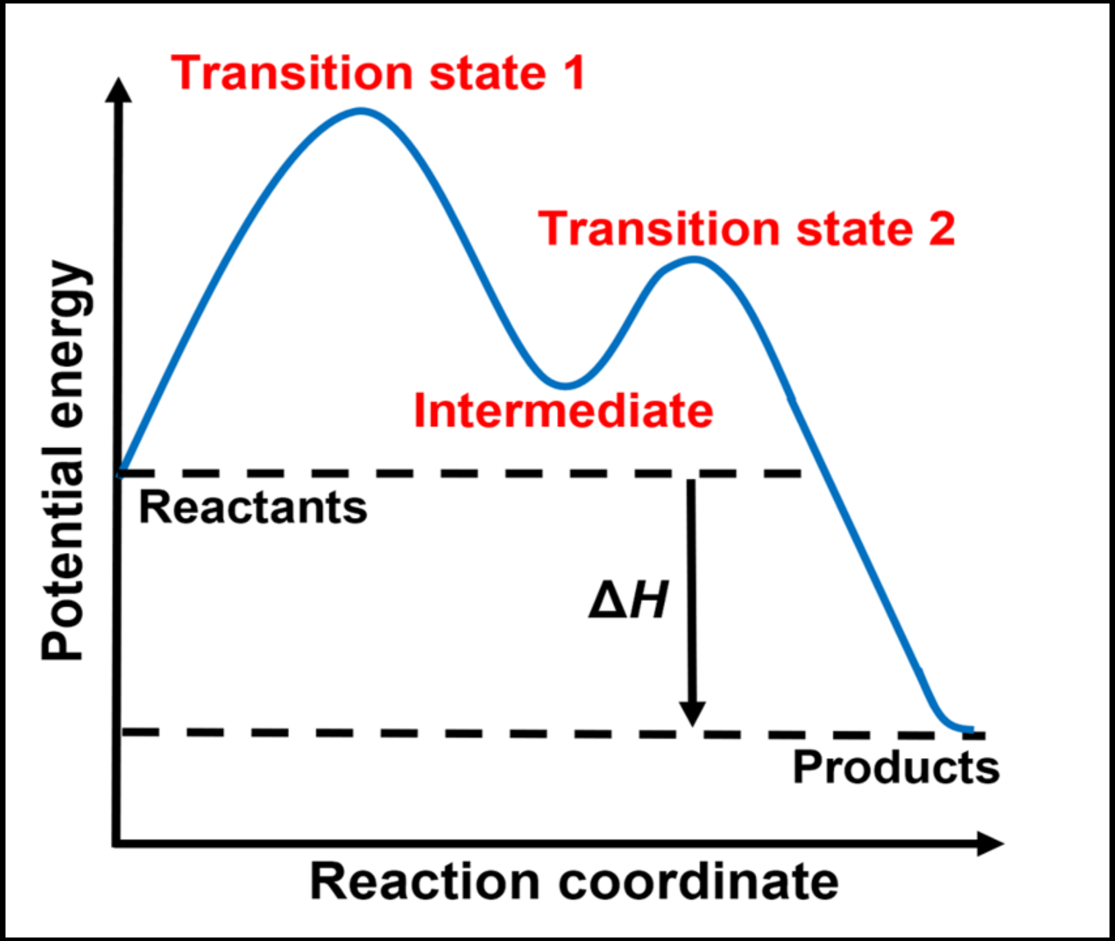
Reaction mechanisms


1st step – slow step
2nd step – fast step
Potential energy
E_a
E_a
Reactants
ΔH
Products
Reaction coordinate

An energy level profile for a two-step reaction is shown. The first step has the highest activation energy so it is the rate-determining step.

Reaction mechanisms



A transition state is a hypothetical state that is mid-way between the reactants and products.

It occurs at the highest point on the energy level profile and is unstable due to its high energy.

Reaction intermediates are more stable.

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Molecularity

Molecularity

Unimolecular – an elementary step that involves one reactant particle.

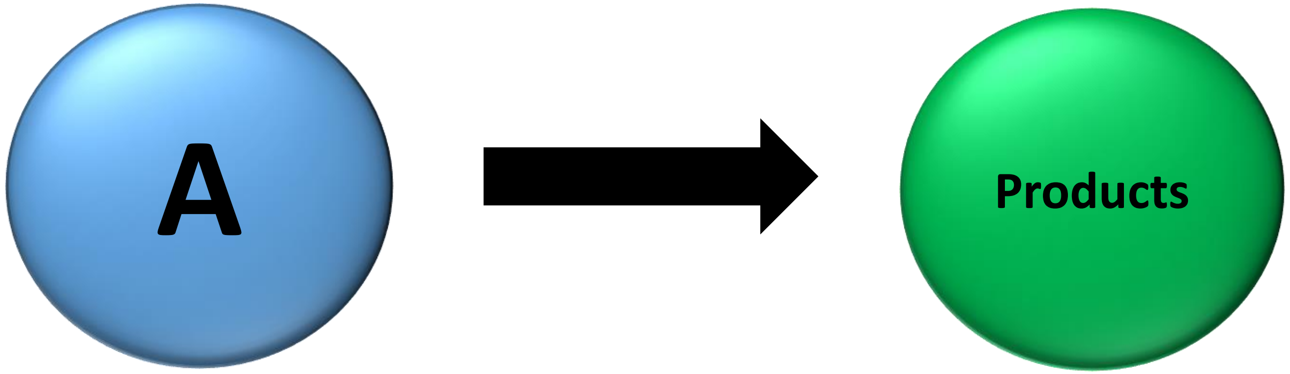
Bimolecular – an elementary step that involves two reactant particles.

Termolecular – an elementary step that involves three reactant particles.

Termolecular steps are rare because of the low probability of three reactant particles colliding with sufficient energy and correct orientation.

Molecularity

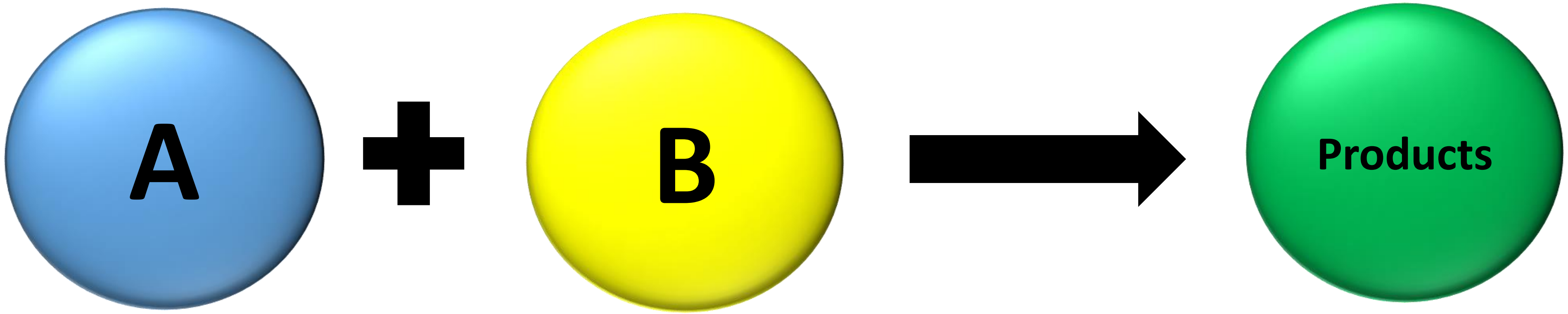
A unimolecular elementary step involves one reactant particle.



$$NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{(g)}$$

Molecularity

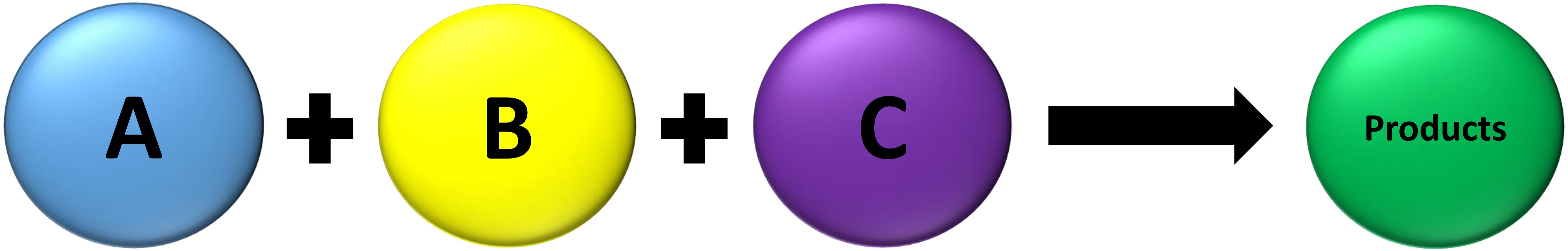
A bimolecular elementary step involves two reactant particles.



$$NO_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$$

Molecularity

A termolecular elementary step involves three reactant particles.



Termolecular steps are rare because of the low probability of three reactant particles colliding with sufficient energy and correct orientation.

Molecularity

The term molecularity indicates the number of reactant particles in an elementary step.

$$2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}$$

Step 1: $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{(g)}$ slow

Step 2: $NO_2Cl_{(g)} + Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$ fast

Step 1: one reactant particle (unimolecular)

Step 2: two reactant particles (bimolecular)

Molecularity

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

Step 1: $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$ slow

Step 2: $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ fast

Step 1: two reactant particles (bimolecular)

Step 2: two reactant particles (bimolecular)

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Rate equations

Rate equations

A rate equation depends on the mechanism of the reaction and can only be determined experimentally.

$$A + B \rightarrow C + D$$

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

k is the rate constant (temperature dependent)
x is the order of reaction with respect to A
y is the order of reaction with respect to B
$x + y$ is the overall order of reaction

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Rate equations

The components of a rate equation can only be determined experimentally:

- Initial rates are calculated using concentration measurements.
- Orders of reaction are calculated using initial rates from several experiments.
- The initial rate and orders of reaction are used to calculate the value of the rate constant *k*.

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Orders of reaction

Orders of reaction

The order of reaction with respect to a particular reactant is the power to which the concentration of a reactant is raised in the rate expression.

$$2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}$$

The rate expression has been experimentally determined to be:

$$\text{rate} = k[NO]^2[H_2]$$

The reaction is second-order with respect to NO and first-order with respect to H_2

Orders of reaction can only be determined experimentally.

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Orders of reaction

If changing the concentration of a reactant has no effect on the rate of reaction, the reaction is zero-order with respect to that reactant.

If changing the concentration of a reactant produces directly proportional changes in the rate of reaction, the reaction is first-order with respect to that reactant.

If changing the concentration of a reactant leads to an increase in the rate of reaction equal to the square of the change, the reaction is second-order with respect to that reactant.

Orders of reaction

$$2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}$$

Experiment	Initial [NO] mol dm^{-3}	Initial [H_2] mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	0.100	0.100	2.53×10^{-6}
2	0.100	0.200	5.05×10^{-6}
3	0.200	0.100	1.01×10^{-5}
4	0.300	0.100	2.28×10^{-5}

$$\text{rate} = k[NO]^2[H_2]$$

Orders of reaction

$$O_{2(g)} + 2NO_{(g)} \rightarrow 2NO_{2(g)}$$

Experiment	Initial $[O_2]$ mol dm^{-3}	Initial [NO] mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.20×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

$$\text{rate} = k[O_2][NO]^2$$

Orders of reaction

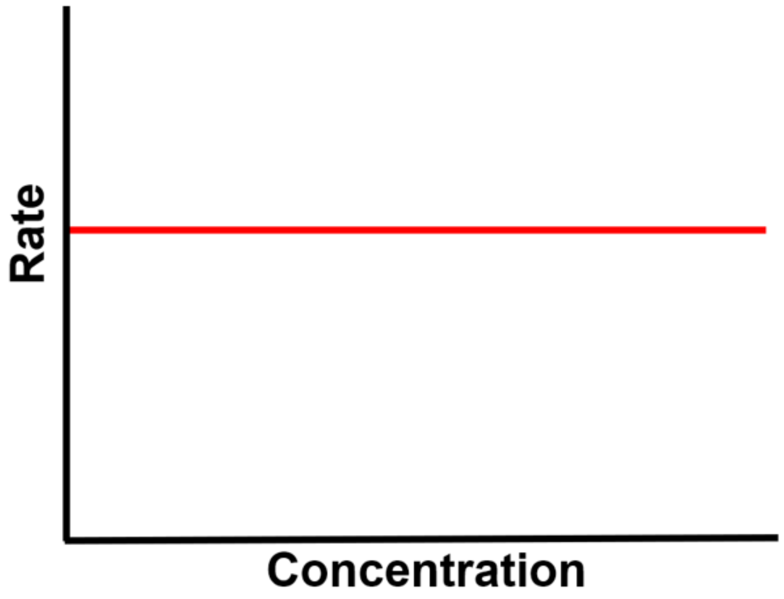
$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

Experiment	Initial $[NO_2]$ mol dm^{-3}	Initial [CO] mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	0.100	0.100	5.00×10^{-3}
2	0.400	0.100	8.00×10^{-2}
3	0.100	0.200	5.00×10^{-3}

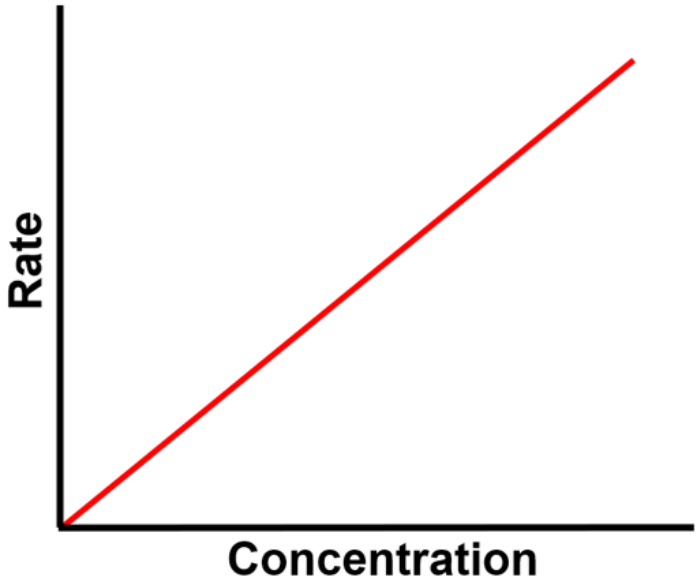
$$\text{rate} = k[NO_2]^2$$

Rate graphs

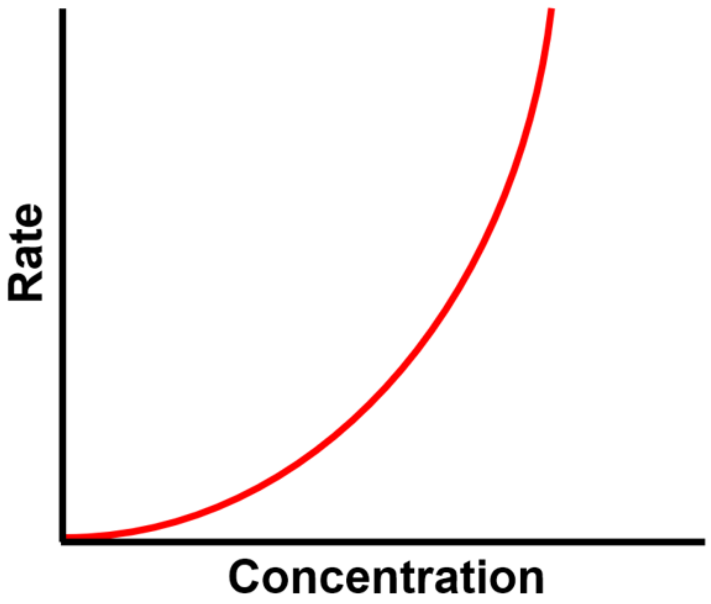
Rate vs concentration (for reactant A)



rate = k



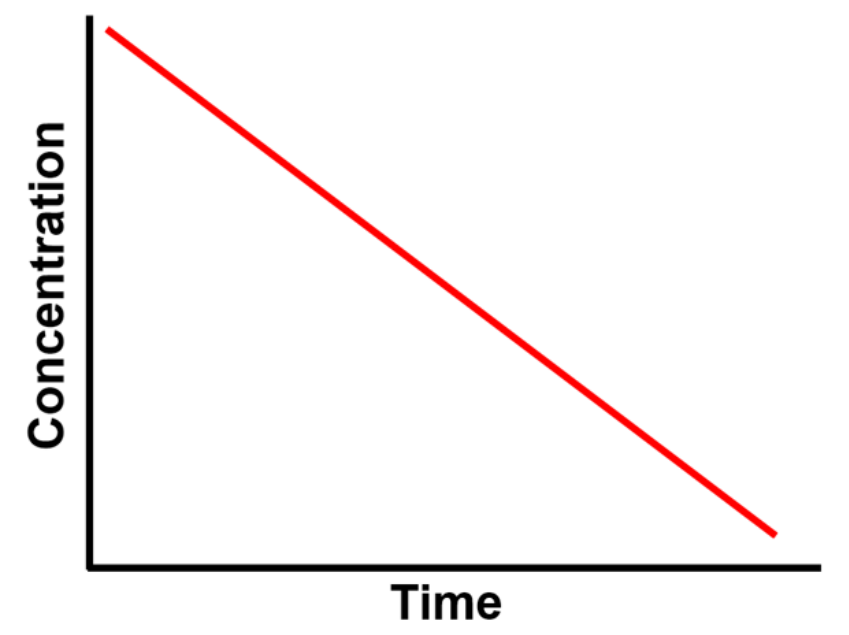
rate = $k[A]$



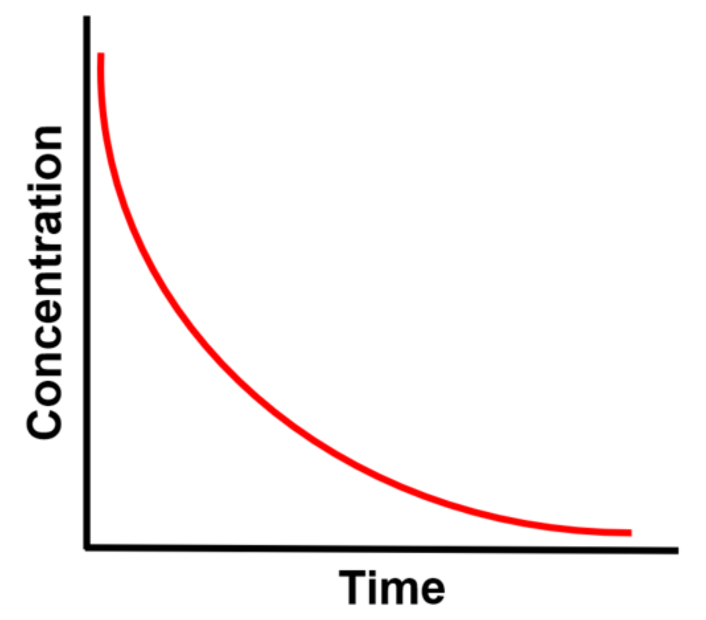
rate = $k[A]^2$

Rate graphs

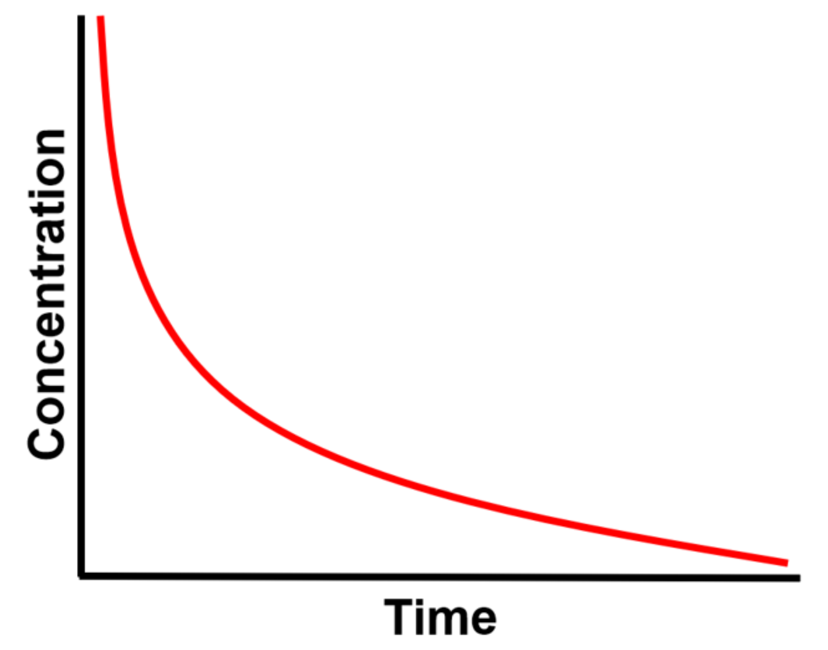
Concentration vs time (for reactant A)



rate = k



rate = $k[A]$



rate = $k[A]^2$

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Rate equations

Rate equations

The rate equation is determined from the slow step of a reaction mechanism.

NO_2Cl decomposes to form NO_2 and Cl_2. The chemical equation for the reaction is shown.

$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

A proposed two-step mechanism is:

Step 1: $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$ slow

Step 2: $NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$ fast

The rate equation is determined from the slow step, therefore:

$$\text{rate} = k[NO_2Cl]$$

Rate equations

Nitrogen monoxide and oxygen react according to the equation shown:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

A proposed two-step mechanism is:

$$\text{Step 1:}\quad NO(g) + O_2(g) \rightleftharpoons NO_3(g) \qquad \text{fast}$$

$$\text{Step 2:}\quad NO_3(g) + NO(g) \rightarrow 2NO_2(g) \qquad \text{slow}$$

The rate equation is determined from the slow step, which is the second step.

Rate equations

Two step mechanism with slow second step:

Step 1: $NO(g) + O_2(g) \rightleftharpoons NO_3(g)$ fast

Step 2: $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$ slow

In this mechanism, NO_3 is an intermediate and cannot be included in the rate equation. The concentration of the intermediate depends on the [NO] and $[O_2]$ in step 1 so the rate equation is:

$$\text{rate} = k[NO]^2[O_2]$$

Note that we include the [NO] in the second step in the rate equation.

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Evaluating reaction mechanisms

Evaluating reaction mechanisms

When evaluating a reaction mechanism, two points must be considered:

1. The sum of the elementary steps must add up to the overall equation.
2. The mechanism must be consistent with the rate equation determined from experimental data.

Evaluating reaction mechanisms

Example: Consider the reaction:

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

The rate equation determined from experimental data is:

$$\text{rate} = k[NO_2][F_2]$$

The proposed two-step reaction mechanism is:

Step 1: $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$ slow

Step 2: $NO_2(g) + F(g) \rightarrow NO_2F(g)$ fast

Evaluating reaction mechanisms

Step 1: $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + \cancel{F(g)}$ slow

Step 2: $NO_2(g) + \cancel{F(g)} \rightarrow NO_2F(g)$ fast

The intermediate, F(g), is canceled out. The elementary steps add up to the overall equation.

The rate equation determined from the slow step is:

$$\text{rate} = k[NO_2][F_2]$$

which is consistent with the rate equation determined from the experimental data.

This is a possible mechanism for the reaction.

Evaluating reaction mechanisms

Consider the reaction:

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

Step 1: $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$ fast

Step 2: $NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$ slow

The rate equation determined from experimental data is:

$$\text{rate} = k[NO]^2[Br_2]$$

Evaluating reaction mechanisms

Step 1: $\mathrm{NO(g) + Br_2(g) \rightleftharpoons \cancel{NOBr_2(g)}}$ fast

Step 2: $\mathrm{\cancel{NOBr_2(g)} + NO(g) \rightarrow 2NOBr(g)}$ slow

The intermediate, $\mathrm{NOBr_2(g)}$, is canceled out. The elementary steps add up to the overall equation.

The rate equation determined from the slow step is:

$$\mathrm{rate = k[NO]^2[Br_2]}$$

which is consistent with the rate equation determined from the experimental data.

This is a possible mechanism for the reaction.

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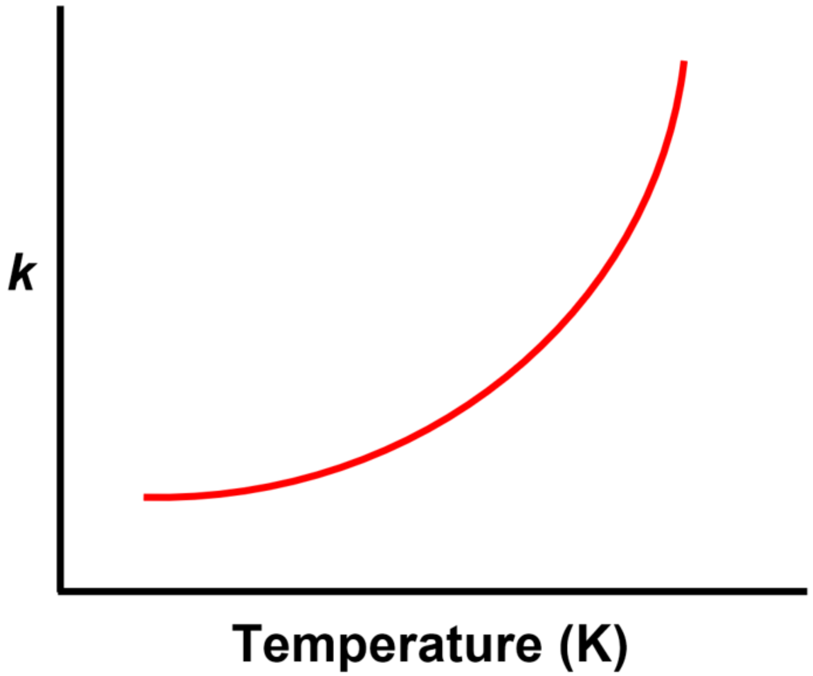
The rate constant *k*

Rate constant *k*

The rate constant *k* is temperature dependent, meaning that it has a specific value at a specific temperature.

The value of the rate constant increases exponentially with an increase in temperature, as shown below.



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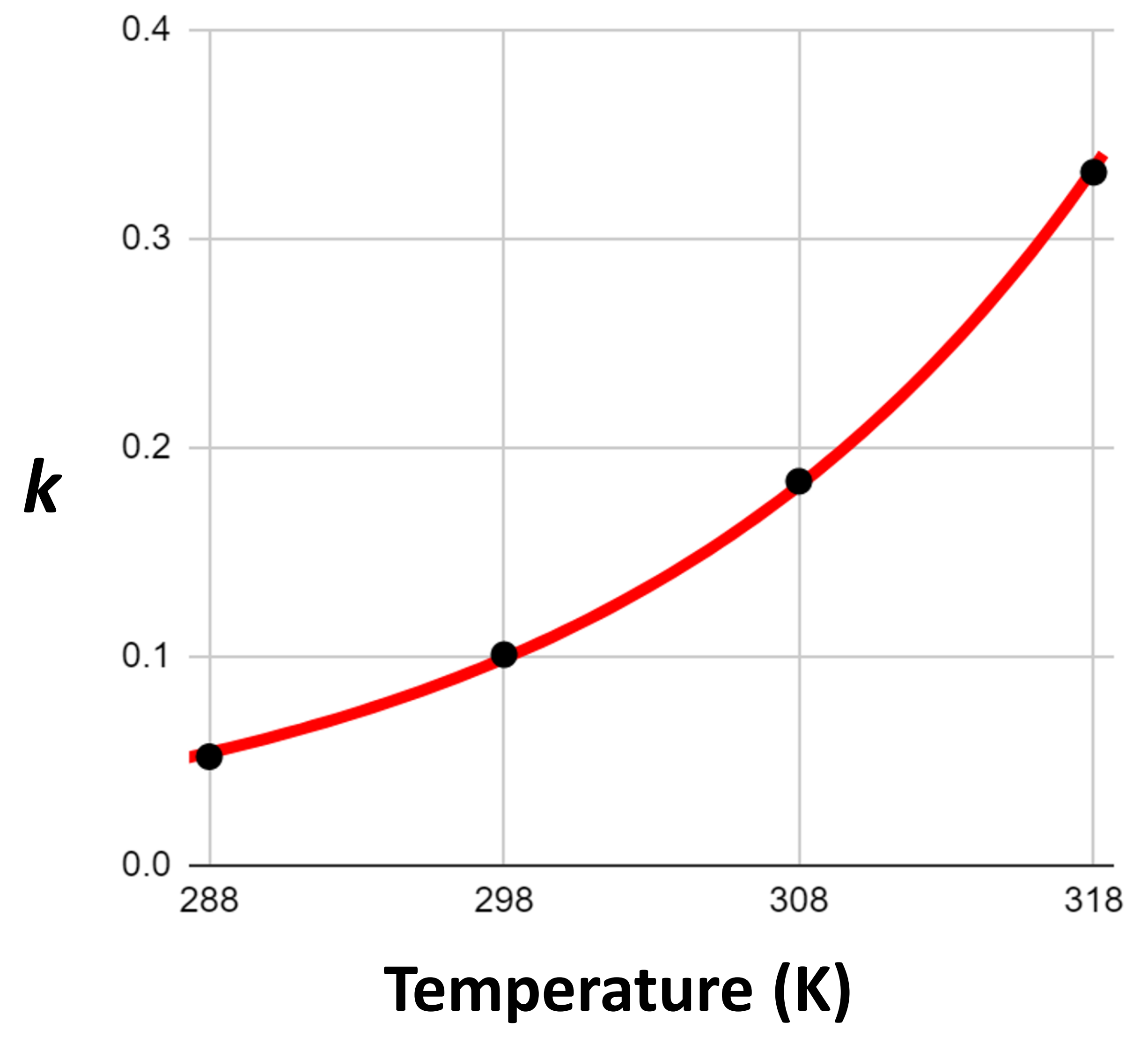
Rate constant *k*

Temperature (K)	Rate constant *k*
288	0.0521
298	0.101
308	0.184
318	0.332



A plot of the rate constant *k* against temperature shows an exponential increase.

Rate constant *k*

$$k = Ae^{\frac{-50000}{8.31\times293}}$$

$$k = Ae^{-20.54}$$

$$k = A(1.20 \times 10^{-9})$$

$$k = Ae^{\frac{-50000}{8.31\times303}}$$

$$k = Ae^{-19.86}$$

$$k = A(2.37 \times 10^{-9})$$

An increase in temperature of 10 K doubles the fraction of particles that have energy equal to or greater than the activation energy.

The value of the rate constant *k* increases which results in an increase in the rate of reaction.

Temperature and *k*

The table below shows the effect of temperature on the fraction of particles with $E \geq E_a$, the value of the rate constant and on the rate of reaction.

Change in temperature	Fraction of particles with $E \geq E_a$	Rate constant k	Rate of reaction
Increase	Increases	Increases	Increases
Decrease	Decreases	Decreases	Decreases

Rate constant *k*

Units of the rate constant *k*

The units of the rate constant k depend on the overall order of reaction, as shown in the table.

Zero-order	First-order	Second-order	Third-order
mol dm^{-3} s^{-1}	s^{-1}	mol^{-1} dm^{3} s^{-1}	mol^{-2} dm^{6} s^{-1}

Rate constant *k*

Calculate the value of the rate constant *k*

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ rate = $k[NO]^2[O_2]$

	Initial [NO] mol dm^{-3}	Initial [O_2] mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
Experiment 1	0.010	0.010	2.5×10^{-5}
Experiment 2	0.020	0.010	1.0×10^{-4}
Experiment 3	0.010	0.020	5.0×10^{-5}

Rate constant *k*

Using the data from experiment 1:

$$\text{rate} = k[NO]^2[O_2]$$

$$2.5 \times 10^{-5} = k\,(0.010)^2\,(0.010)$$

$$k = 2.5 \times 10^{-5} / 1.0 \times 10^{-6}$$

$$k = 25\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

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The Arrhenius equation

The Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

k : the rate constant

A : the Arrhenius constant (frequency factor or pre-exponential factor)

$e^{\frac{-E_a}{RT}}$: the fraction of particles that have energy equal to or greater than the E_a at temperature T

The Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

k : depend on reaction

A : same as k

E_a : J mol^{-1}

R : 8.31 J K^{-1} mol^{-1}

T : kelvin (K)

The Arrhenius equation

The Arrhenius constant, *A*, takes into account the frequency of collisions with the correct orientation for the reaction to occur.

$$A = Zp$$

$$\mathrm{Z} = \text{collision frequency}$$

$$p = \text{steric factor}$$

The Arrhenius equation

The Arrhenius constant, *A*, takes into account the frequency of collisions with the correct orientation for the reaction to occur.

$$NO_{(g)} + NO_{3(g)} \rightarrow 2NO_{2(g)}$$

Steric factor, $p = 0.006$

Only 6 out of every 1000 collisions have the correct orientation for a reaction to occur.

The Arrhenius equation

$$f = e^{\frac{-E_a}{RT}}$$

f : the fraction of collisions with energy equal to or greater than the activation energy for the reaction.

E_a (J mol^{-1})	*f* (298 K)
50000	1.70×10^{-9}
75000	7.03×10^{-14}
100000	2.90×10^{-18}

The Arrhenius equation

$$f = e^{\frac{-E_a}{RT}}$$

f : the fraction of collisions with energy equal to or greater than the activation energy for the reaction.

Temperature (K)	*f* (E_a = 50000 J mol^{-1})
298	1.70 × 10^{-9}
308	3.29 × 10^{-9}
318	6.12 × 10^{-9}

The Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

Higher temperatures and lower activation energies result in a higher value of the rate constant *k* and an increased rate of reaction.

Lower temperatures and higher activation energies result in a lower value of the rate constant *k* and a decreased rate of reaction.

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Calculating activation energy, E_a

Calculating activation energy

$$k = Ae^{\frac{-E_a}{RT}}$$

k : the rate constant

A : the Arrhenius constant (frequency factor or pre-exponential factor)

$e^{\frac{-E_a}{RT}}$: the fraction of particles that have energy equal to or greater than the E_a

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Calculating activation energy

$$k = Ae^{\frac{-E_a}{RT}}$$

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

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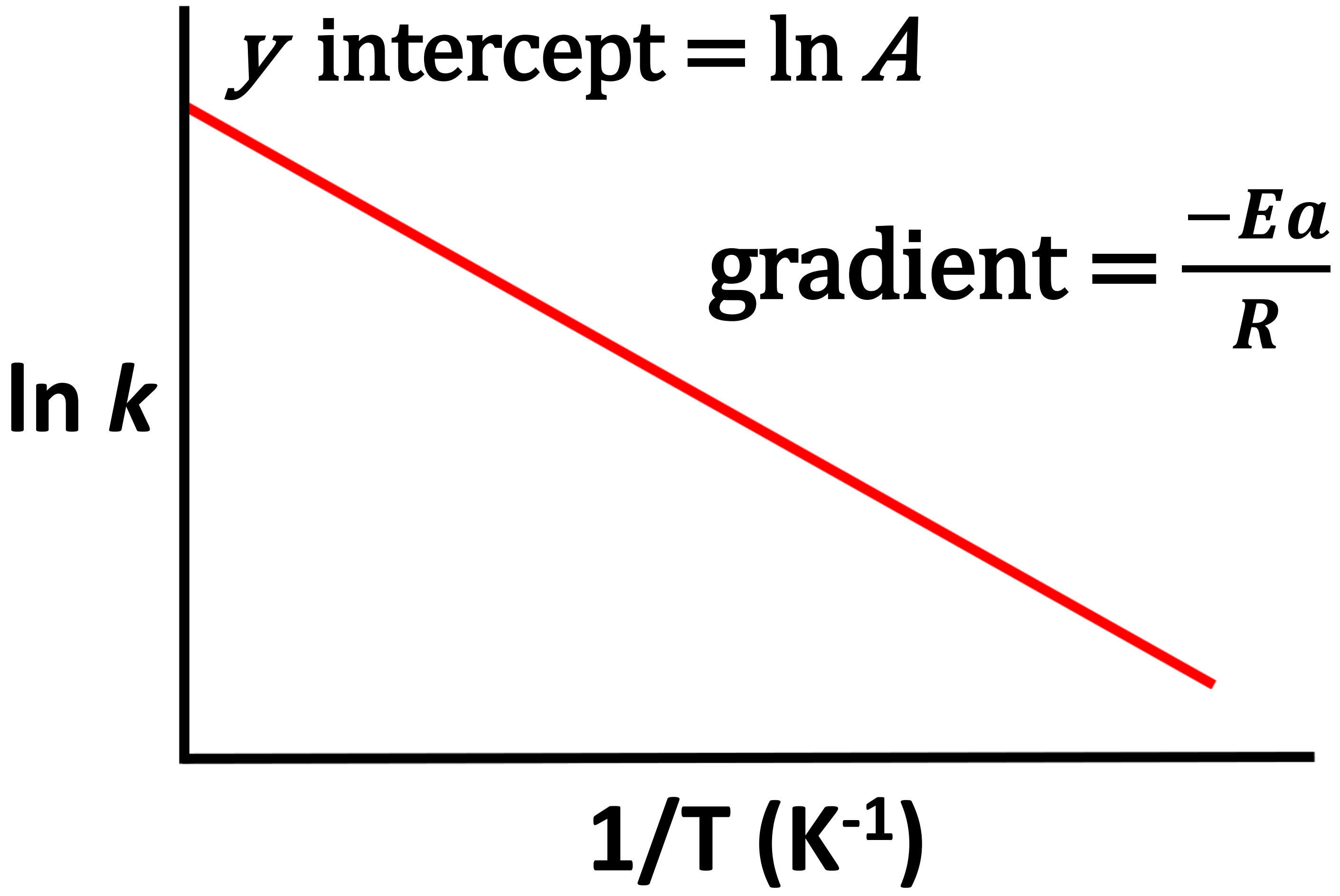
Calculating activation energy

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

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

$$y = mx + c$$

Calculating activation energy



A graph of ln k against 1/T gives a straight line with the gradient $-E_a/R$

$$-E_a\ (\text{J mol}^{-1}) = \text{gradient (K)} \times 8.31\ (\text{J K}^{-1}\ \text{mol}^{-1})$$

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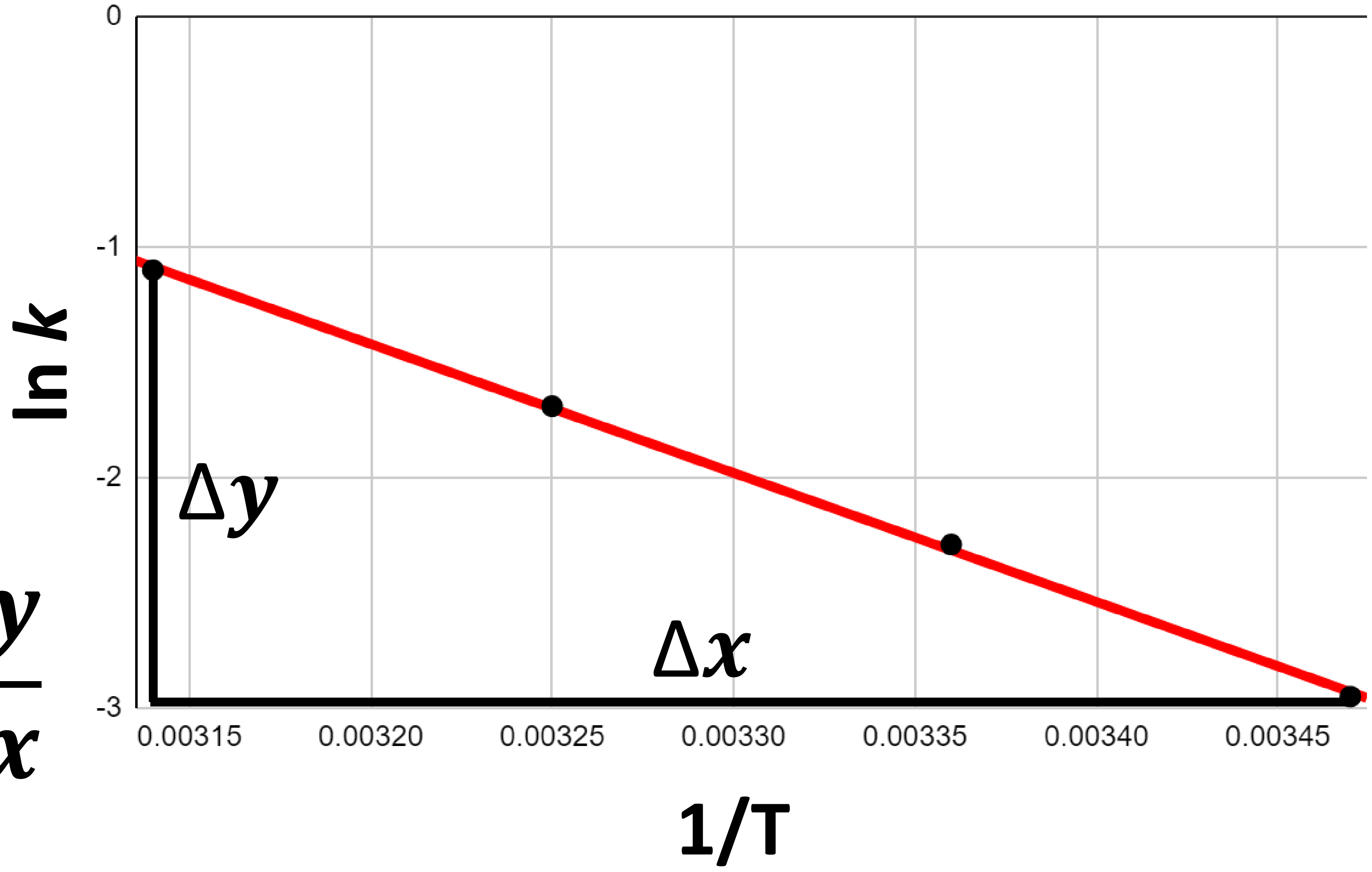
Calculating activation energy

ln *k*	1/T
-2.95	0.00347
-2.29	0.00336
-1.69	0.00325
-1.1	0.00314

$$\text{gradient} = \frac{\Delta y}{\Delta x}$$



Calculating activation energy

$$\text{gradient} = \frac{-1.84}{3.30 \times 10^{-4}} = -5576\ \text{K}$$

$$-E_a = -5576\ \text{K} \times 8.31\ \text{J K}^{-1}\text{mol}^{-1}$$

$$E_a = 46337\ \text{J mol}^{-1}$$