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**Tutorials for IB Chemistry**

**Topic 16**

**Kinetics HL**

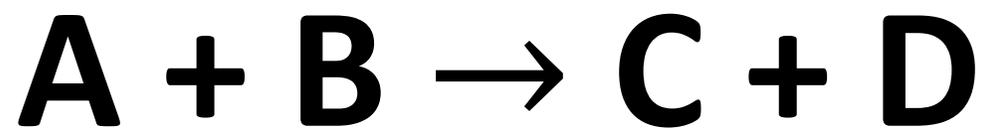
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**Rate expressions**

# Rate expressions

A rate expression (rate law or rate equation) expresses the rate of reaction as a function of reactant concentrations and temperature.



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

**$k$  is the rate constant (temperature dependent)**

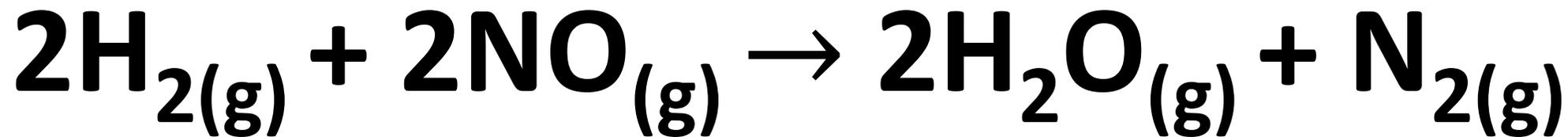
**$x$  is the order of reaction with respect to A**

**$y$  is the order of reaction with respect to B**

**$x + y$  is the overall order of reaction**

# Rate expressions

Consider the reaction:



The rate expression has been experimentally determined to be:

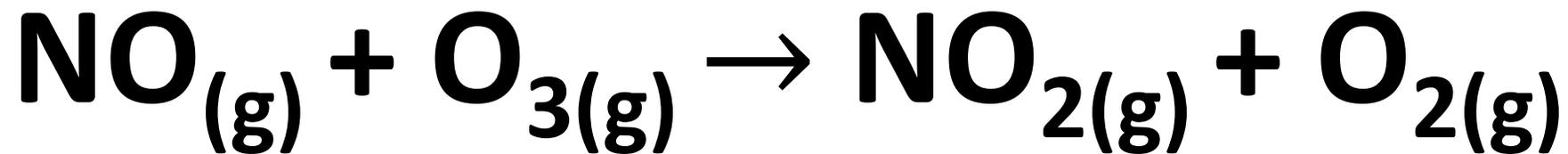
$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The reaction is second-order with respect to NO and first-order with respect to H<sub>2</sub>.

The reaction is third order overall.

# Rate expressions

Consider the reaction:



The rate expression has been experimentally determined to be:

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

The reaction is first-order with respect to both NO and O<sub>3</sub>.

The reaction is second order overall.

# Rate expressions

The rate constant  $k$  is a constant that is specific for a given reaction at a given temperature (temperature dependent).

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

**A** – Arrhenius constant (frequency factor)

**e** – Euler's number

**$E_a$**  – activation energy

**R** – universal gas constant

**T** – temperature in K

# Rate expressions

The components of a rate expression 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  $k$ .

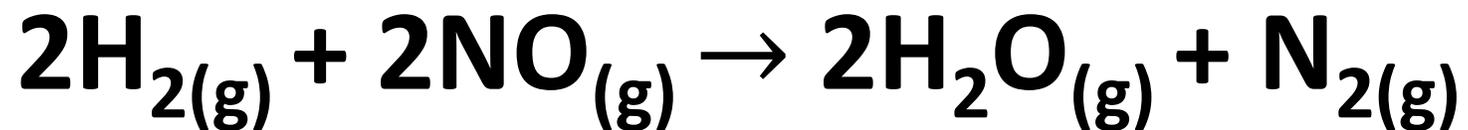
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**Orders of reaction**

# 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.



The rate expression has been experimentally determined to be:

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The reaction is second-order with respect to NO and first-order with respect to H<sub>2</sub>

Orders of reaction can only be determined experimentally.

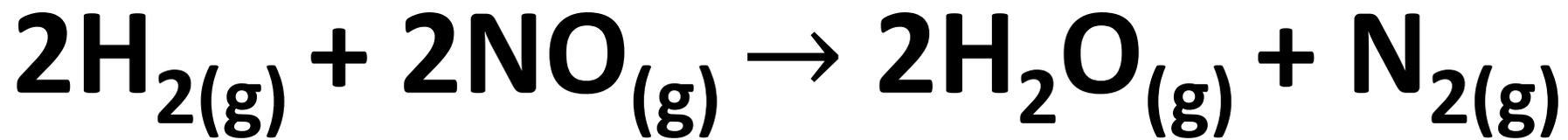
# Orders of reaction

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.

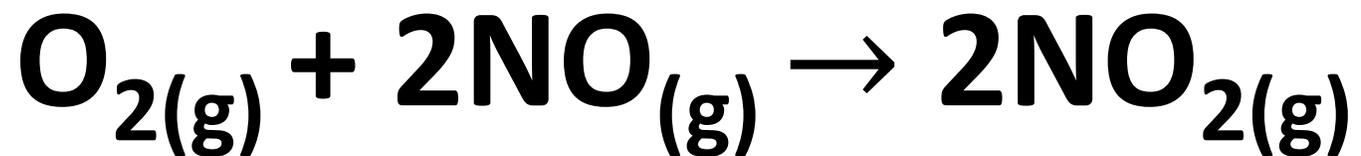
# Orders of reaction



Experiment	Initial [NO] mol dm <sup>-3</sup>	Initial [H <sub>2</sub> ] mol dm <sup>-3</sup>	Initial rate mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.100	0.100	$2.53 \times 10^{-6}$
2	0.100	0.200	$5.05 \times 10^{-6}$
3	0.200	0.100	$1.01 \times 10^{-5}$
4	0.300	0.100	$2.28 \times 10^{-5}$

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

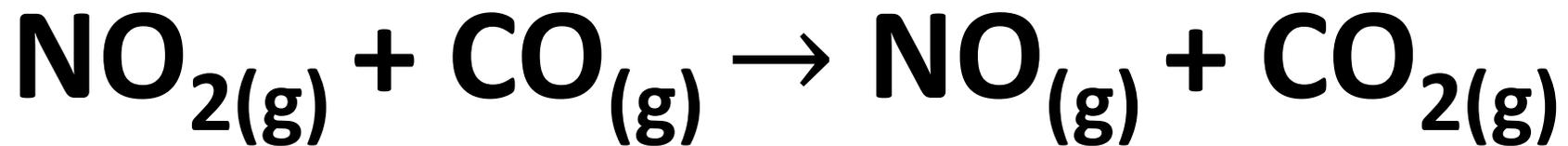
# Orders of reaction



Experiment	Initial [O <sub>2</sub> ] mol dm <sup>-3</sup>	Initial [NO] mol dm <sup>-3</sup>	Initial rate mol dm <sup>-3</sup> s <sup>-1</sup>
1	1.10 × 10 <sup>-2</sup>	1.30 × 10 <sup>-2</sup>	3.20 × 10 <sup>-3</sup>
2	2.20 × 10 <sup>-2</sup>	1.30 × 10 <sup>-2</sup>	6.40 × 10 <sup>-3</sup>
3	1.10 × 10 <sup>-2</sup>	2.60 × 10 <sup>-2</sup>	12.8 × 10 <sup>-3</sup>
4	3.30 × 10 <sup>-2</sup>	1.30 × 10 <sup>-2</sup>	9.60 × 10 <sup>-3</sup>

$$\text{rate} = k[\text{O}_2][\text{NO}]^2$$

# Orders of reaction



Experiment	Initial $[\text{NO}_2]$ $\text{mol dm}^{-3}$	Initial $[\text{CO}]$ $\text{mol dm}^{-3}$	Initial rate $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.100	0.100	$5.00 \times 10^{-3}$
2	0.400	0.100	$8.00 \times 10^{-2}$
3	0.100	0.200	$5.00 \times 10^{-3}$

$$\text{rate} = k[\text{NO}_2]^2$$

# 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.

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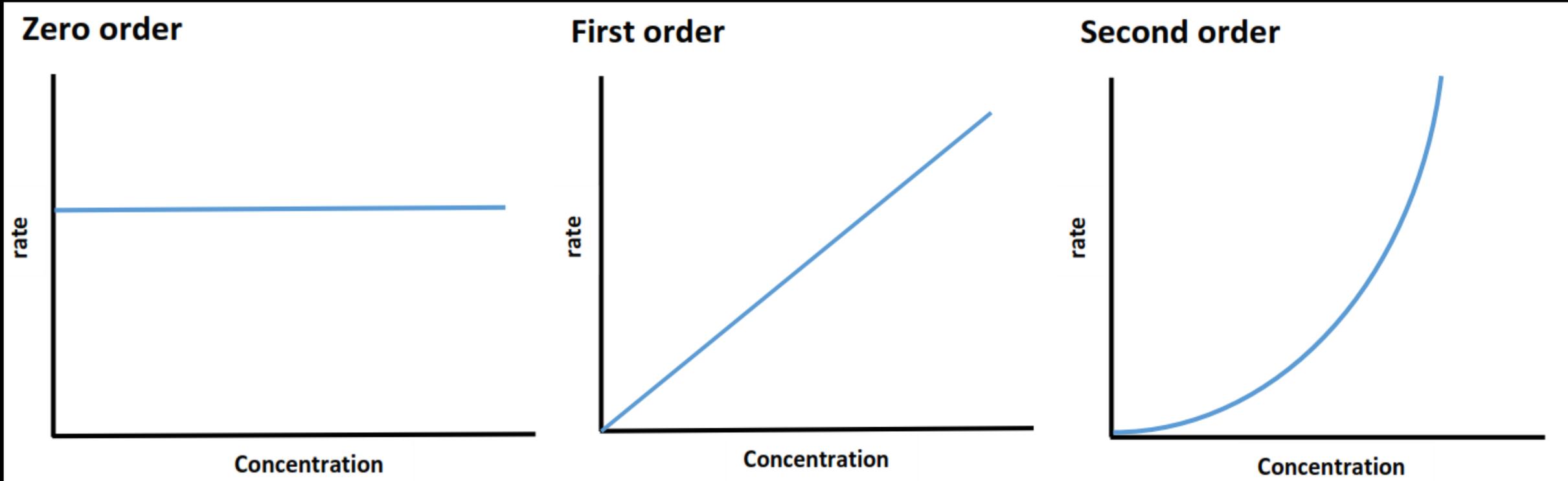
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**Rate graphs**

# Rate graphs

## Rate vs concentration (for reactant A)



$\text{rate} = k$

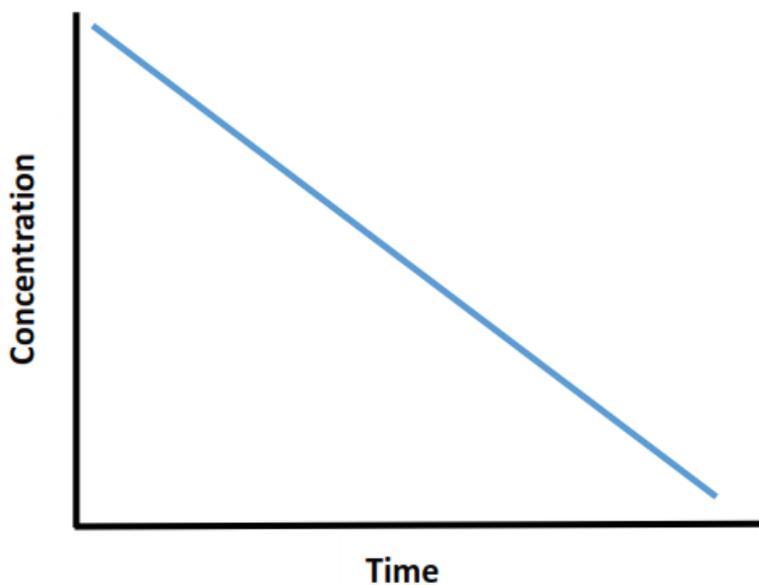
$\text{rate} = k[A]$

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

# Rate graphs

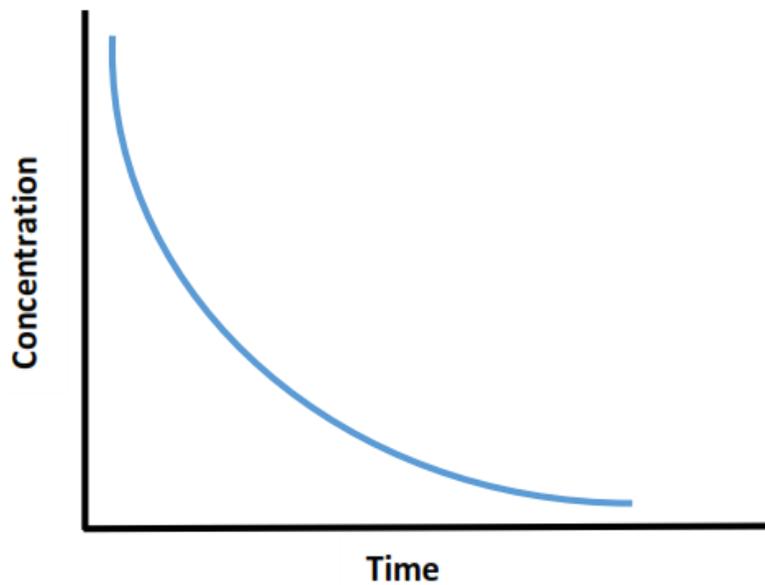
## Concentration vs time (for reactant A)

Zero order



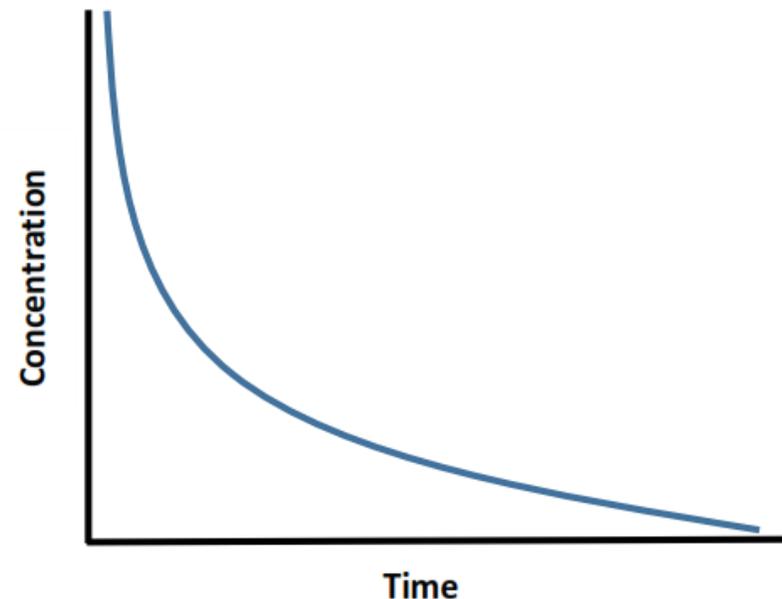
$$\text{rate} = k$$

First order



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

Second order



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

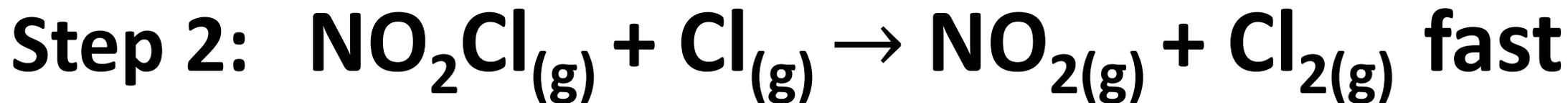
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**Reaction mechanisms**

# Reaction mechanisms

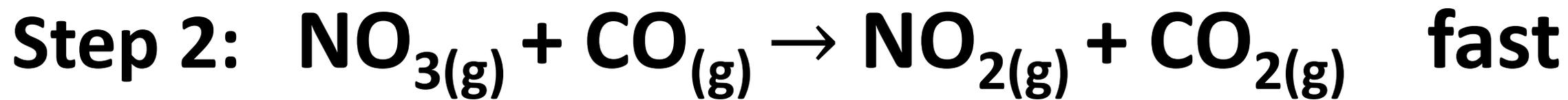
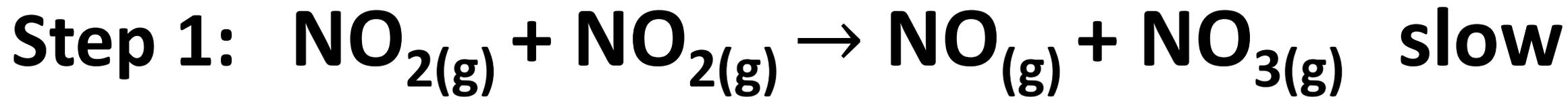
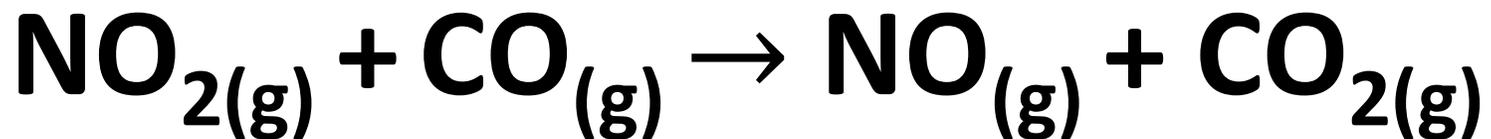
Chemical reactions can occur in a series of steps called elementary steps; the sequence of elementary steps is the reaction mechanism.



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

# Reaction mechanisms

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



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

# Reaction mechanisms

When considering a proposed reaction mechanism, the following three 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.
- The elementary steps must be reasonable (unimolecular and bimolecular steps are more common, termolecular steps are unlikely).

# Reaction mechanisms



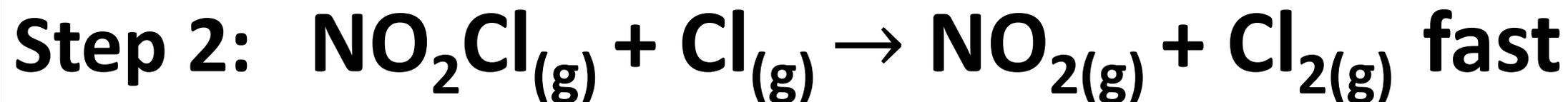
The  $\text{Cl}_{(g)}$  is a reaction intermediate; it is produced in one step and consumed in the next step.

The elementary steps add up to the overall equation.

Step 1 is unimolecular (one reactant particle).

Step 2 is bimolecular (two reactant particles).

# Reaction mechanisms



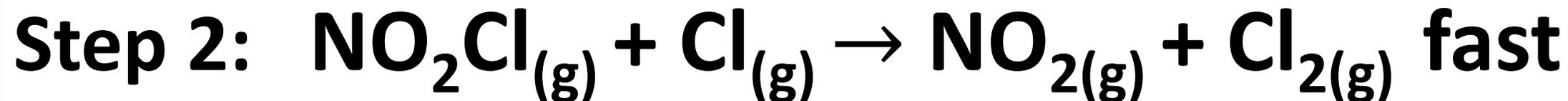
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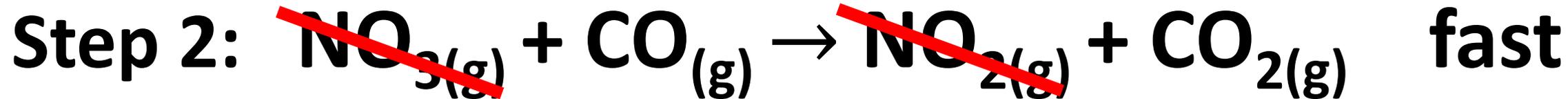
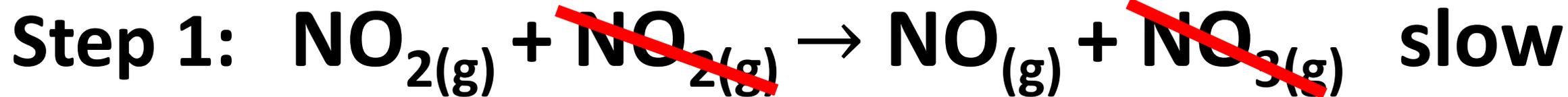
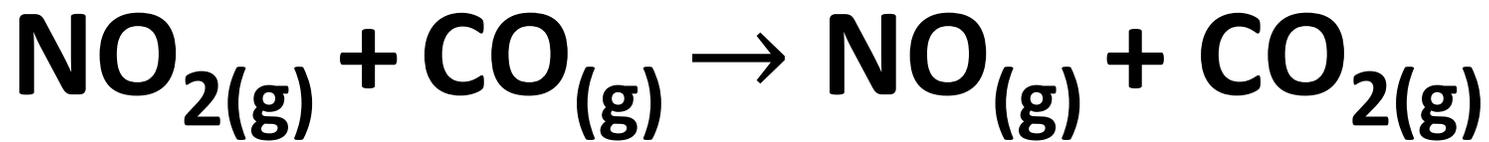
# Reaction mechanisms



$$\text{rate} = k[\text{NO}_2\text{Cl}]$$

The reaction was found to be first-order with respect to  $\text{NO}_2\text{Cl}$  (from experimental data).

# Reaction mechanisms

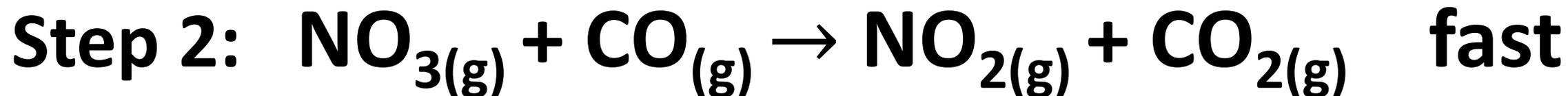
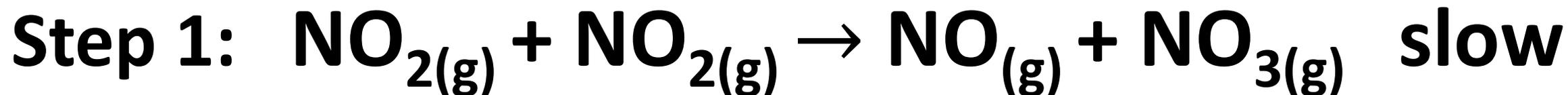
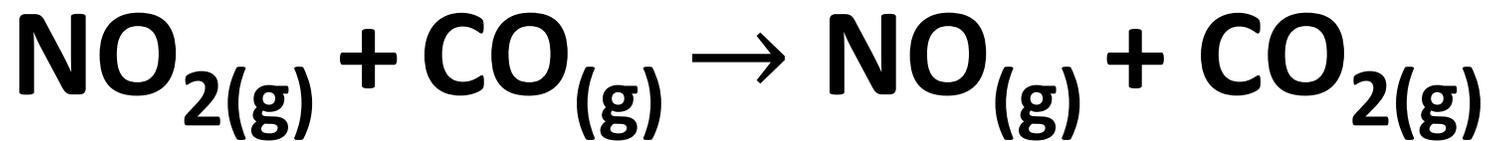


The elementary steps add up to the overall equation.

$$\text{rate} = k[\text{NO}_2]^2$$

The reaction was found to be second-order with respect to  $\text{NO}_2$  (from experimental data).

# Reaction mechanisms

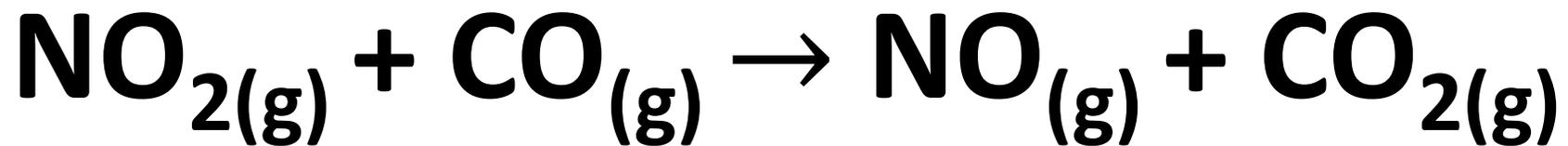


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The reaction was found to be second-order with respect to  $\text{NO}_2$  (from experimental data).

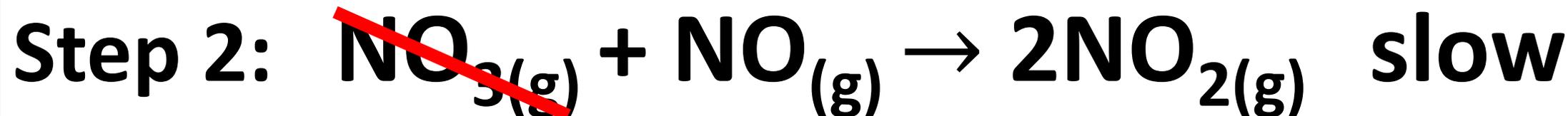
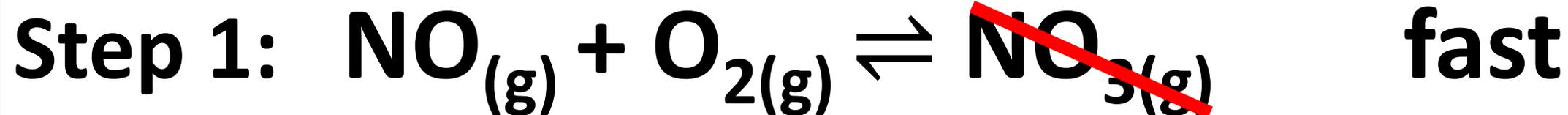
# Orders of reaction



Experiment	Initial $[\text{NO}_2]$ $\text{mol dm}^{-3}$	Initial $[\text{CO}]$ $\text{mol dm}^{-3}$	Initial rate $\text{mol dm}^{-3} \text{ s}^{-1}$
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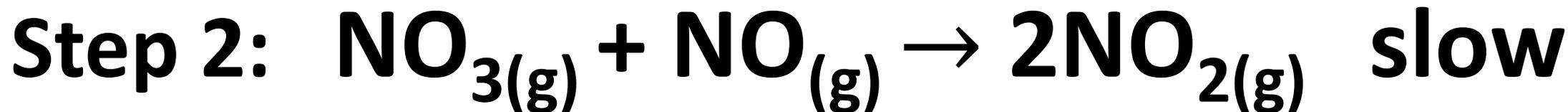
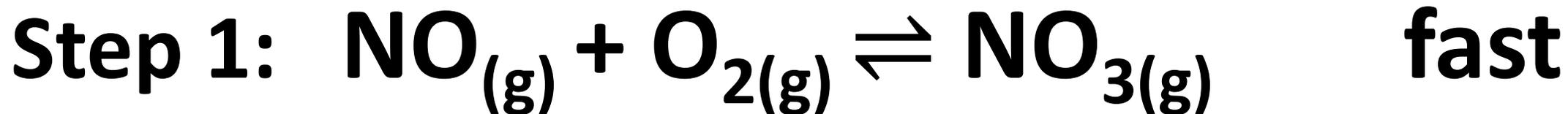
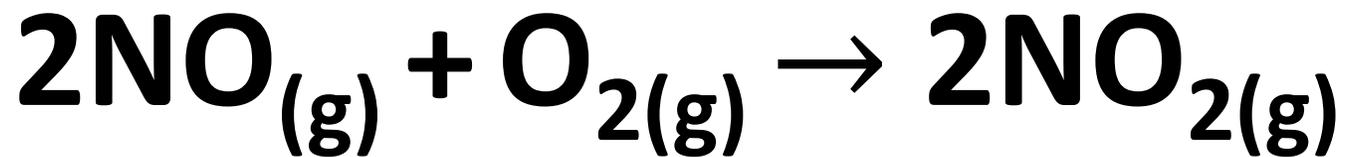
$$\text{rate} = k[\text{NO}_2]^2$$

# Reaction mechanisms



Elementary steps add up to the overall equation.  
Both steps are bimolecular.

# Reaction mechanisms

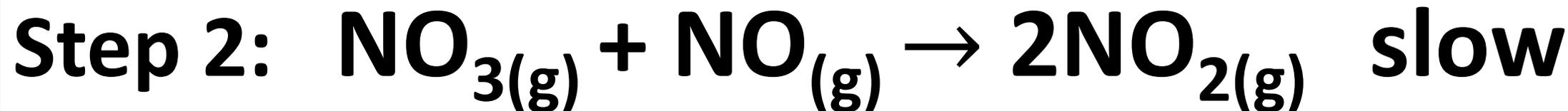
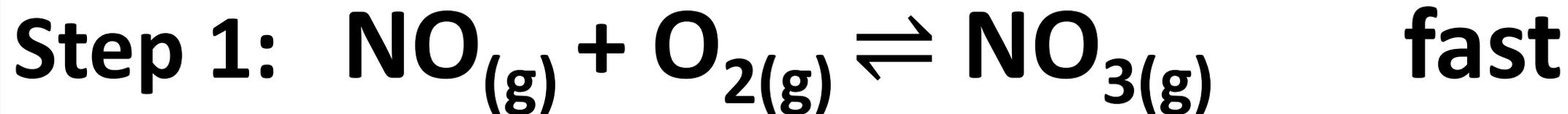
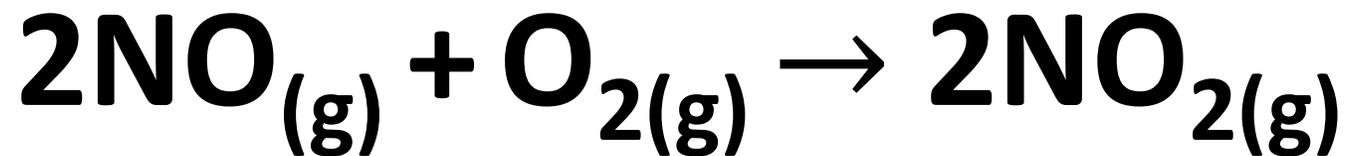


$$\text{rate}_{1(\text{fwd})} = k_1[\text{NO}][\text{O}_2]$$

$$\text{rate}_{1(\text{rev})} = k_{-1}[\text{NO}_3]$$

$$\text{rate}_2 = k_2[\text{NO}_3][\text{NO}]$$

# Reaction mechanisms

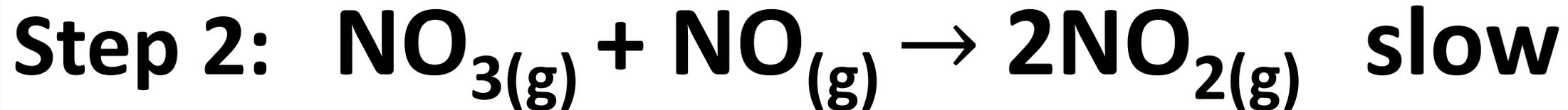
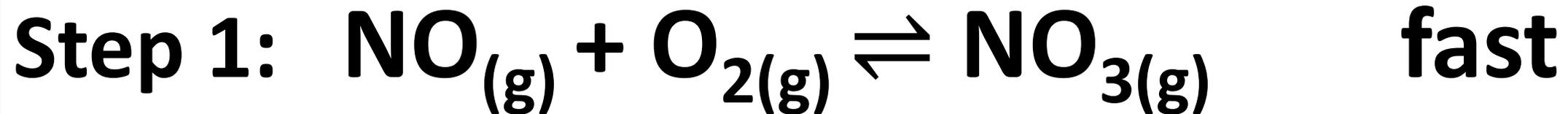


$$\text{rate}_{1(\text{fwd})} = \text{rate}_{1(\text{rev})}$$

$$k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3]$$

$$[\text{NO}_3] = \frac{k_1}{k_{-1}} [\text{NO}][\text{O}_2]$$

# Reaction mechanisms

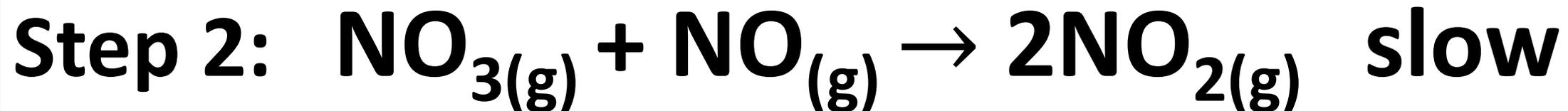
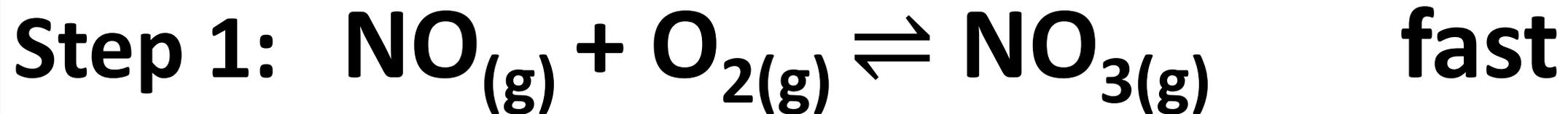
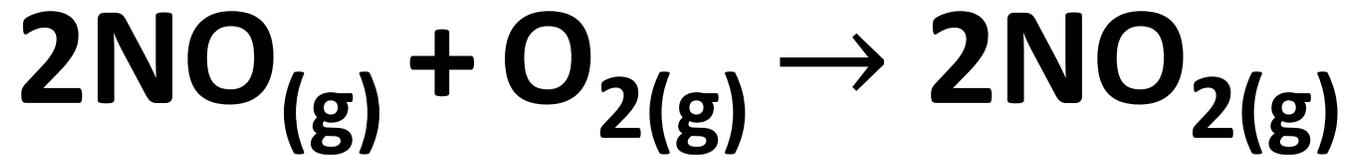


$$\text{rate}_2 = k_2[\text{NO}_3][\text{NO}]$$

$$\text{rate}_2 = k_2 \left( \frac{k_1}{k_{-1}} [\text{NO}][\text{O}_2] \right) [\text{NO}]$$

$$\text{rate}_2 = k_2 [\text{NO}]^2 [\text{O}_2]$$

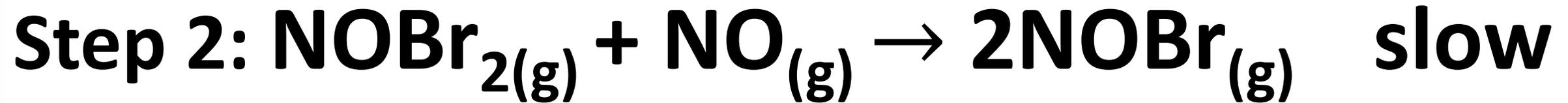
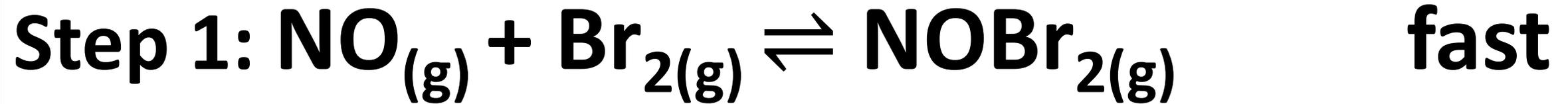
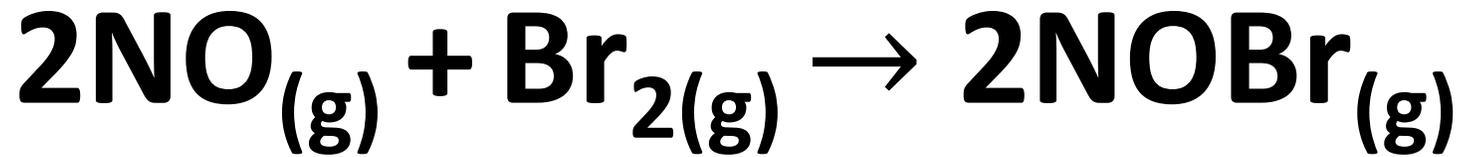
# Reaction mechanisms



The reaction was found to be second-order with respect to NO and first-order with respect to O<sub>2</sub> (from experimental data).

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

# Reaction mechanisms

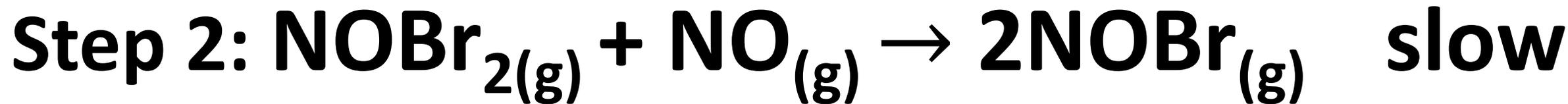
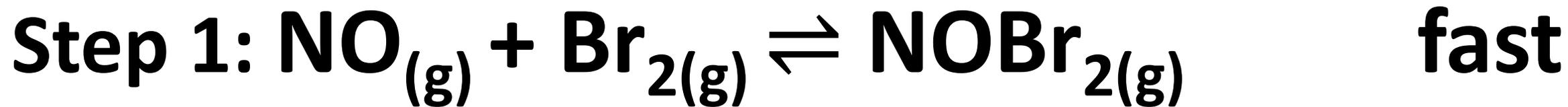
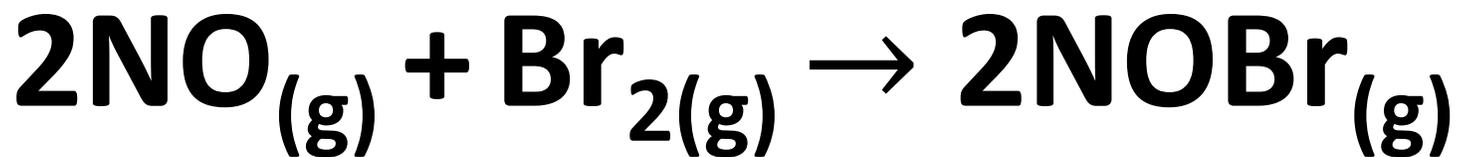


$$\text{rate}_{1(\text{fwd})} = k_1[\text{NO}][\text{Br}_2]$$

$$\text{rate}_{1(\text{rev})} = k_{-1}[\text{NOBr}_2]$$

$$\text{rate}_2 = k_2[\text{NOBr}_2][\text{NO}]$$

# Reaction mechanisms

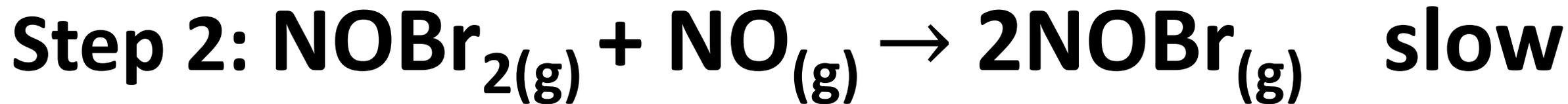
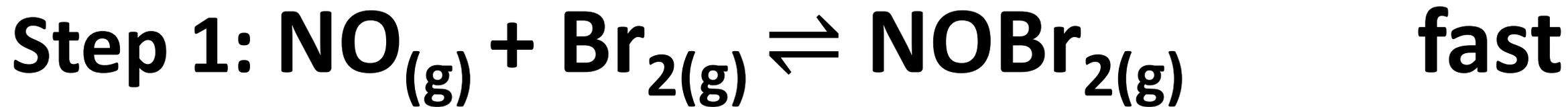
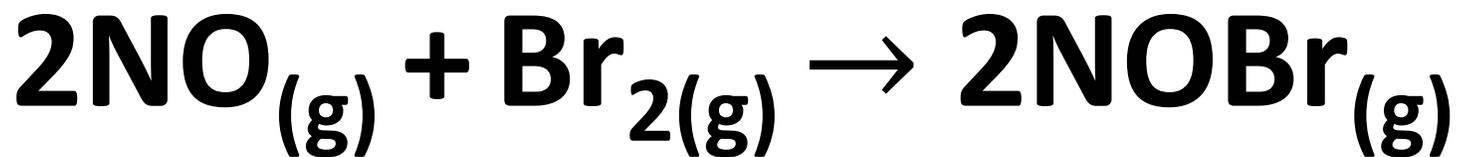


$$\text{rate}_{1(\text{fwd})} = \text{rate}_{1(\text{rev})}$$

$$k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2]$$

# Reaction mechanisms

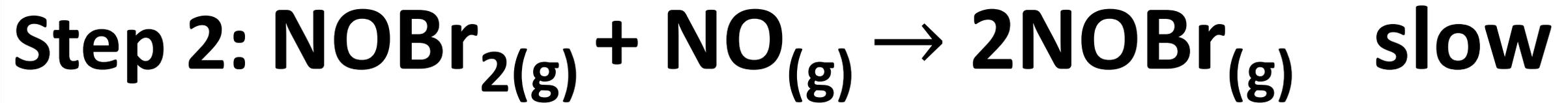
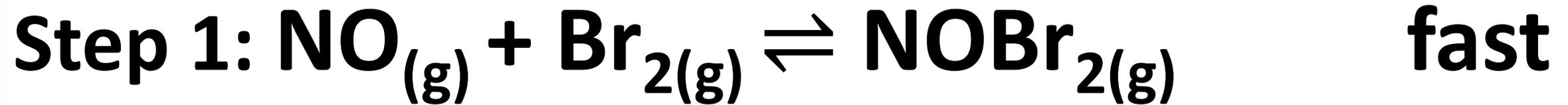
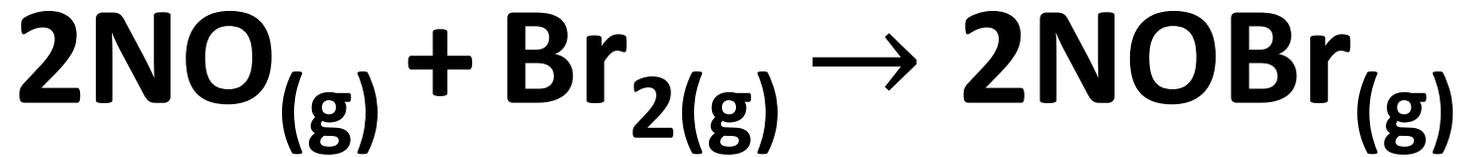


$$\text{rate}_2 = k_2[\text{NOBr}_2][\text{NO}]$$

$$\text{rate}_2 = k_2 \left( \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2] \right) [\text{NO}]$$

$$\text{rate}_2 = k_2 [\text{NO}]^2 [\text{Br}_2]$$

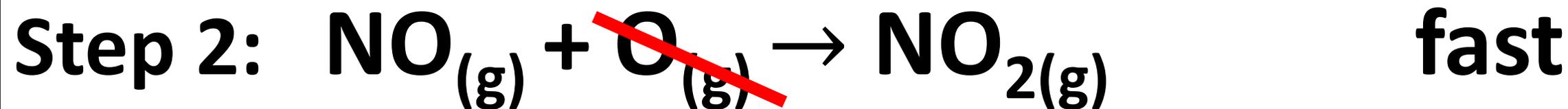
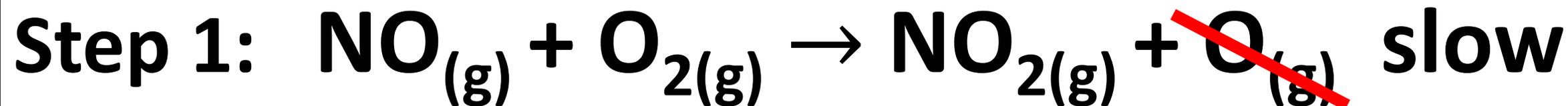
# Reaction mechanisms



The reaction was found to be second-order with respect to NO and first-order with respect to Br<sub>2</sub> (from experimental data).

$$\text{rate} = k[\text{NO}]^2[\text{Br}_2]$$

# Reaction mechanisms



$$\text{rate} = k[\text{NO}_2]^2[\text{O}_2]$$

$$\text{rate} = k[\text{NO}_2][\text{O}_2]$$

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**Molarity**

# Molecularity

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

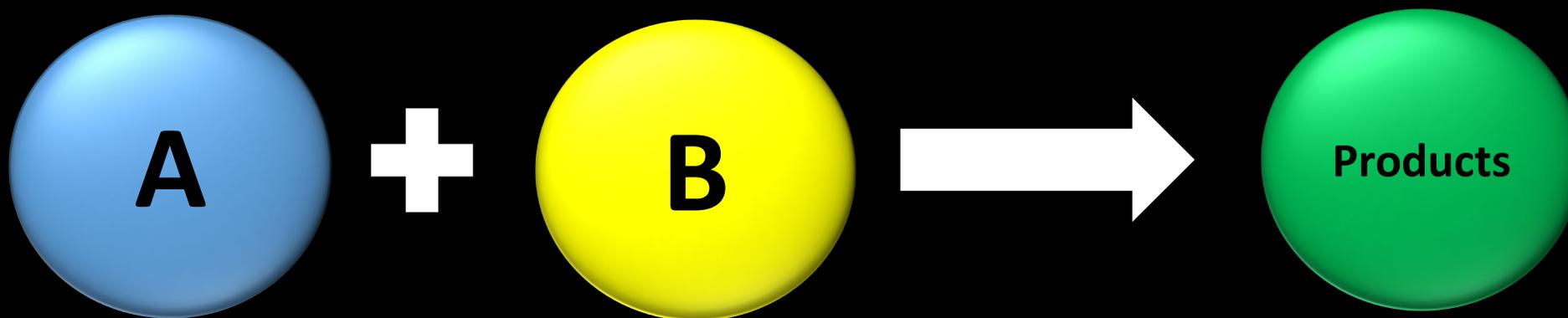
Unimolecular – an elementary step that involves a single reactant particle.



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

# Molecularity

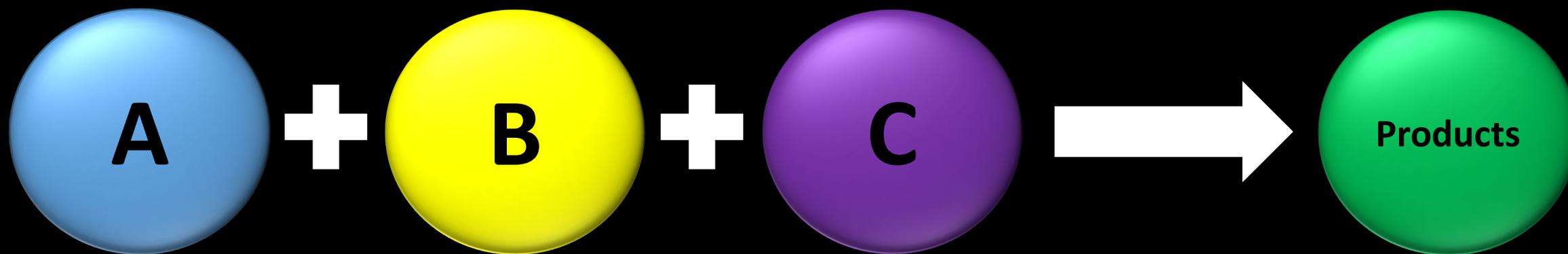
Bimolecular – an elementary step that involves two reactant particles.



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

# Molecularity

Termolecular – an elementary step that involves three reactant particles (very low probability).



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

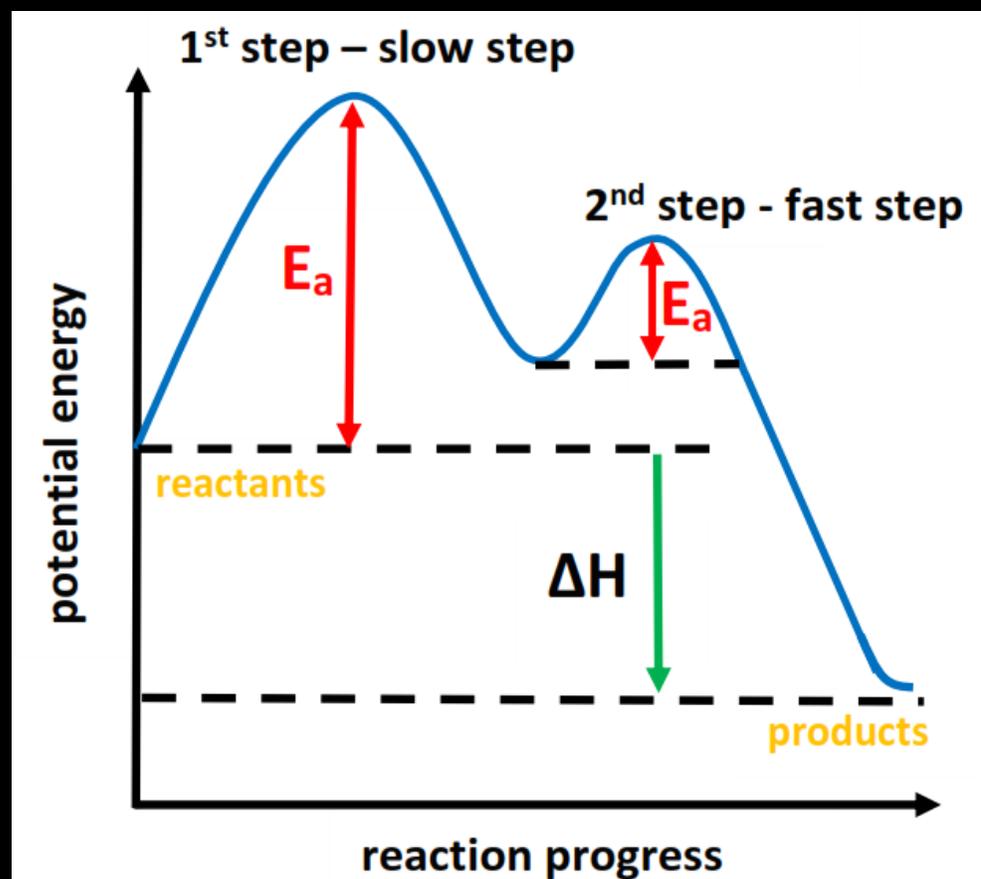
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**Rate-determining step**

# Rate-determining step

Reactions can occur in more than one step and it is the slowest step that determines the rate of reaction.



The 1<sup>st</sup> step has the highest activation energy, therefore it is the slowest step.

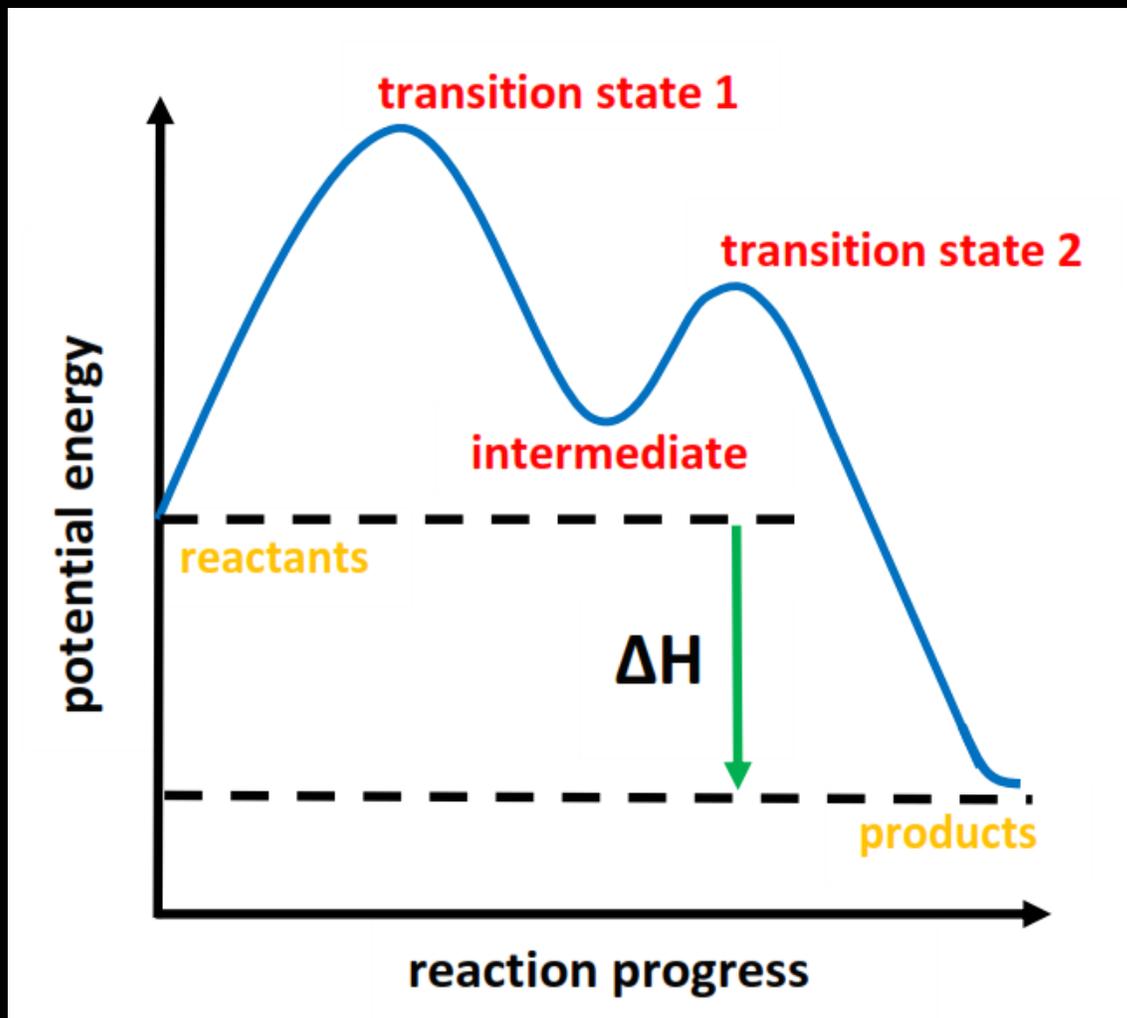
The rate of reaction depends on the speed of this step – it is the rate-determining step.

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**Reaction intermediates  
and transition states**

# Energy level profiles



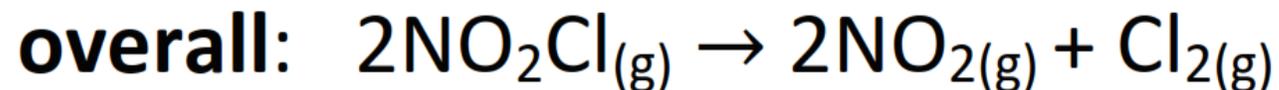
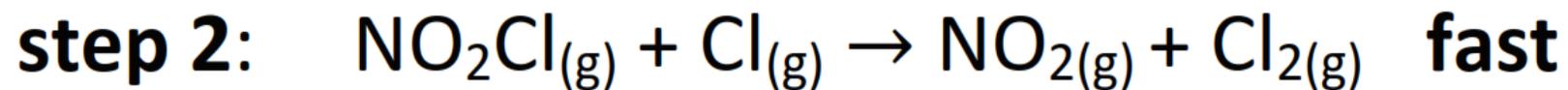
Transition state theory describes a hypothetical transition state that exists between reactants and products during a chemical reaction. The species formed in the transition state is called the activated complex.

Reaction intermediates are species in multi-step reactions which are produced and consumed in the elementary steps therefore do not appear in the overall chemical equation.

# Rate determining step

The rate-determining step (RDS), which is the slowest step in a chemical reaction, determines the overall rate of reaction.

The RDS is the step in a reaction mechanism that has the highest activation energy.



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**The Arrhenius equation**

# Arrhenius equation

The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.

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

**A** – Arrhenius constant (frequency factor)

**$E_a$**  – activation energy ( $\text{J mol}^{-1}$ )

**R** – gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )

# Arrhenius equation

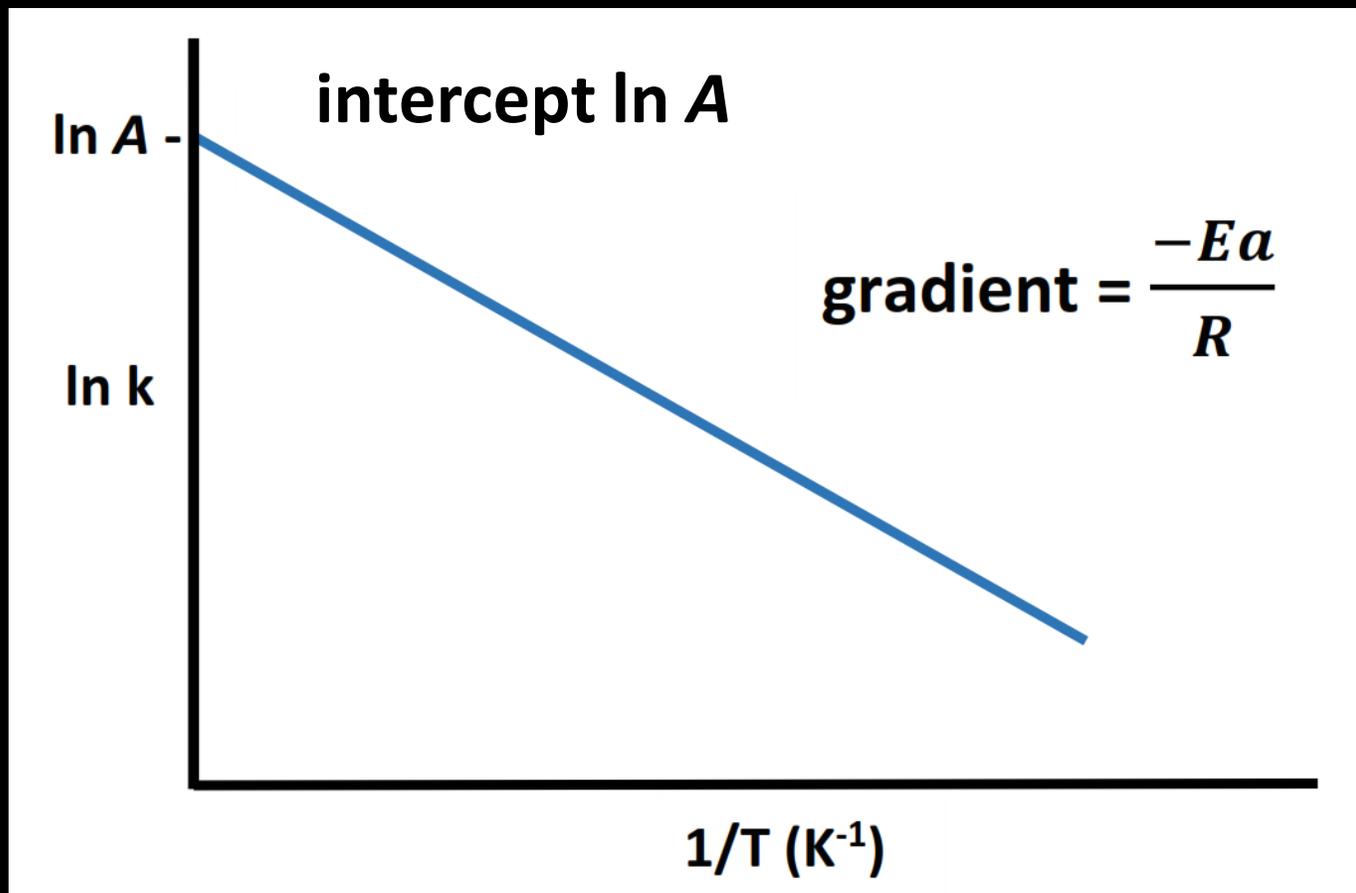
The Arrhenius constant ( $A$  – the frequency factor or pre-exponential factor) takes into account the frequency of collisions with the correct orientation for the reaction to occur.

The Arrhenius equation is often expressed in its logarithmic form:

$$\ln k = (-E_a/RT) + \ln A$$

$$y = mx + c$$

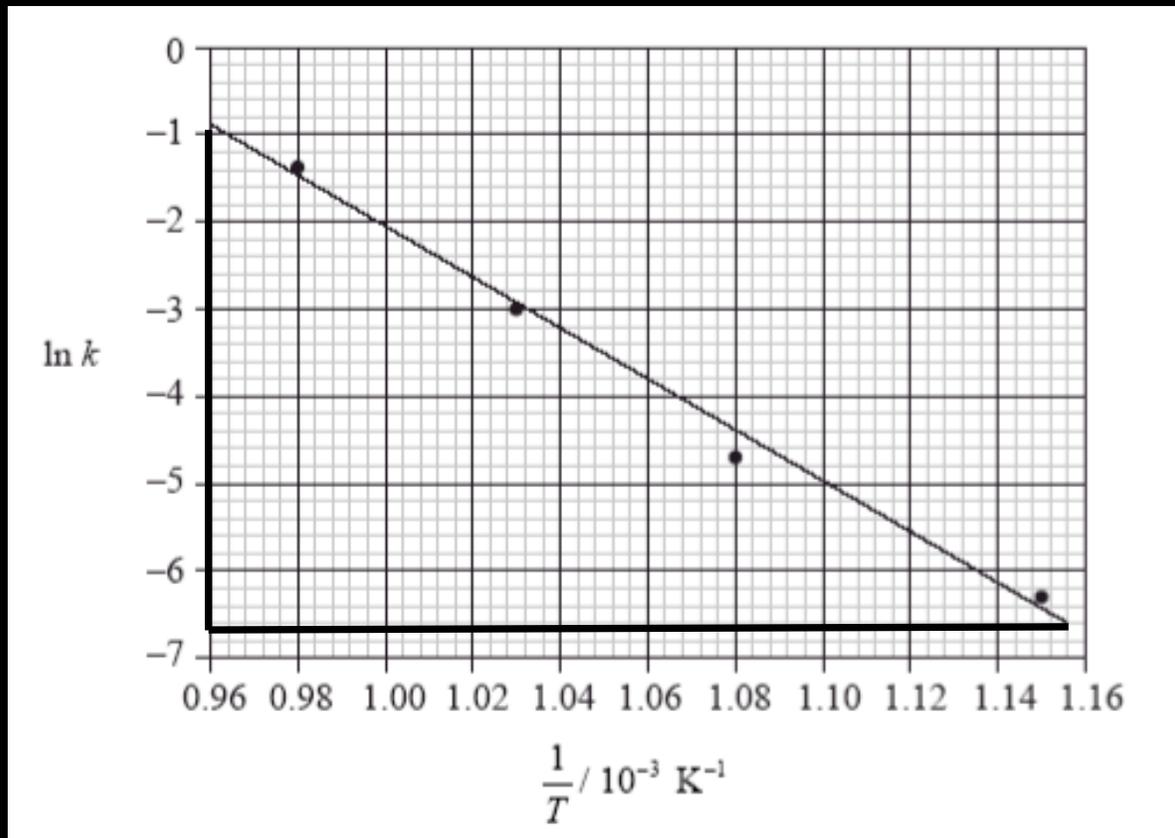
# Arrhenius equation



A graph of  $\ln k$  (y-axis) against  $1/T$  (x-axis) gives a straight line with the gradient  $-E_a/R$

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

# Arrhenius equation



$$\text{gradient} = -E_a/R$$

$$-30000 \text{ (K)} = -E_a/R$$

$$E_a = 30000 \times 8.31$$

$$E_a = 249300 \text{ Jmol}^{-1}$$

$$E_a = 249 \text{ kJmol}^{-1}$$

$$\frac{\Delta y}{\Delta x} = \frac{-5.5}{0.196 \times 10^{-3}} = -30000 \text{ K}$$

# Arrhenius equation

The activation energy can also be calculated from values of the rate constant  $k$  at two different temperatures.

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

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**Effect of increasing  
temperature on the rate  
constant  $k$**

# Temperature and $k$

For most reactions, an increase in temperature of 10 K (10°C) doubles the rate of reaction.

In the Arrhenius equation  $e^{(-E_a/RT)}$  is the fraction of molecules which have energy equal to or greater than activation energy at a particular temperature.

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

The Arrhenius constant ( $A$ ) is approximately constant for such a small increase in temperature (10 K).

# Temperature and $k$

$$k = Ae^{(-50000/8.31 \times 293)}$$

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

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

$$k = Ae^{(-50000/8.31 \times 303)}$$

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

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

An increase in temperature of 10 K (10°C) doubles the fraction of molecules that have energy equal to or greater than the activation energy.

An increase in temperature increases the value of the rate constant  $k$  and therefore the rate of reaction.

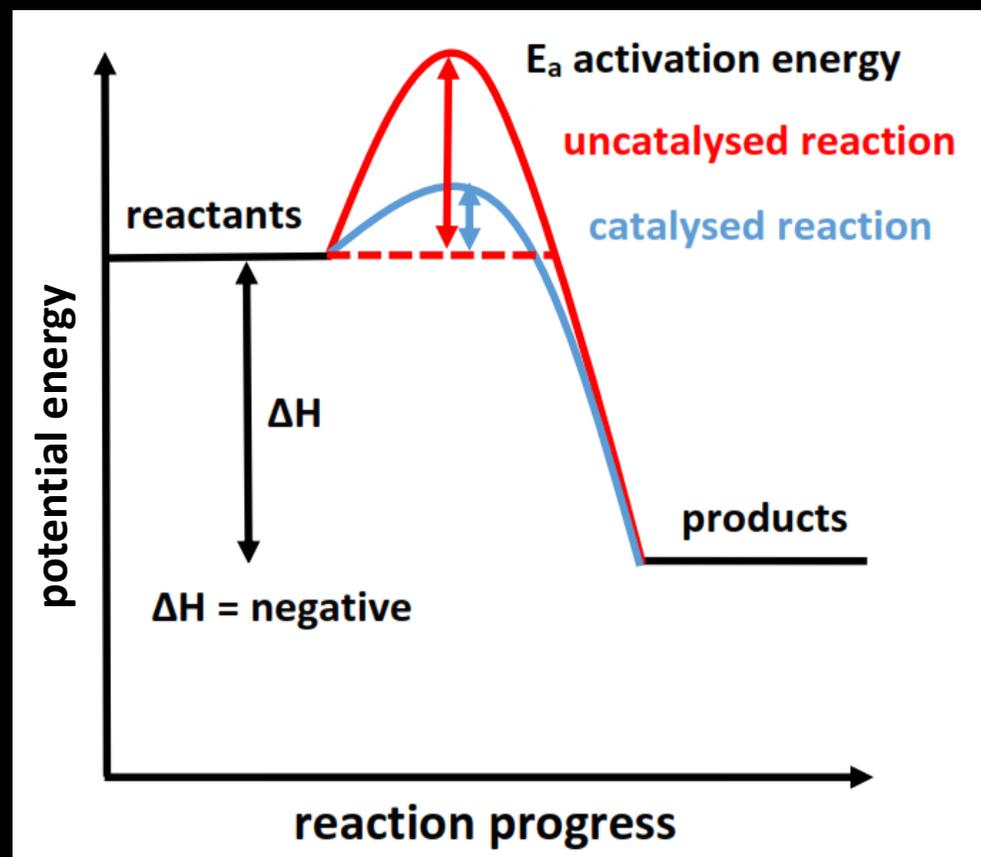
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**Catalysts**

# Catalysts

Catalysts increase the rate of a chemical reaction by providing an alternative reaction pathway with lower activation energy ( $E_a$ )



Catalysts alter the reaction mechanism, introducing a step with lower activation energy.

A catalyst is not consumed during the course of the reaction.

By lowering the activation energy, the rate constant is increased (at the same temperature) relative to the uncatalysed reaction.

# Catalysts

without catalyst

$$k = Ae^{(-50000/8.31 \times 303)}$$

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

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

with catalyst

$$k = Ae^{(-25000/8.31 \times 303)}$$

$$k = Ae^{(-9.93)}$$

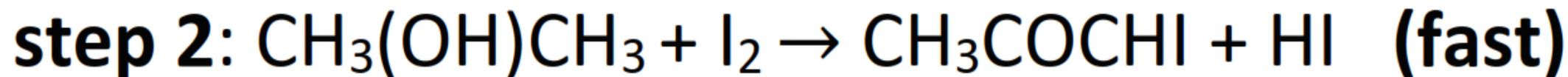
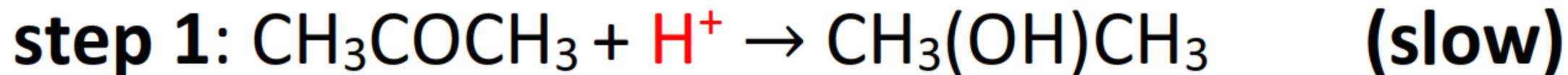
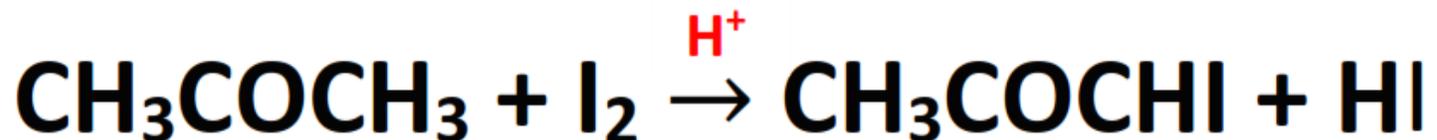
$$k = A (4.87 \times 10^{-5})$$

At the same temperature, the catalysed reaction has a higher fraction of molecules with energy equal to or greater than the activation energy which increases the rate of reaction.

The rate constant  $k$  also increases.

# Catalysts

Catalysts are involved in the rate determining step but do not appear in the overall equation.



$$\text{rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$$