

Kinetics HL

IB CHEMISTRY HL

Answers

| | | | | | |
|---|--|---|--|--|---|
| <div>25</div> <div>Mn</div> <div>Manganese 54.938045</div> | <div>16</div> <div>S</div> <div>Sulfur 32.065</div> | <div></div> <div>J</div> <div></div> | <div>6</div> <div>C</div> <div>Carbon 12.0107</div> | <div>2</div> <div>He</div> <div>Helium 4.002602</div> | <div>25</div> <div>Mn</div> <div>Manganese 54.938045</div> |
|---|--|---|--|--|---|

16.1 Rate expression and reaction mechanism

Understandings:

- Reactions may occur by more than one step and the slowest step determines the rate of reaction (rate determining step/RDS).
- The molecularity of an elementary step is the number of reactant particles taking part in that step.
- The order of a reaction can be either integer or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step.
- Rate equations can only be determined experimentally.
- The value of the rate constant (k) is affected by temperature and its units are determined from the overall order of the reaction.
- Catalysts alter a reaction mechanism, introducing a step with lower activation energy.

Applications and skills:

- Deduction of the rate expression for an equation from experimental data and solving problems involving the rate expression.
- Sketching, identifying, and analysing graphical representations for zero, first and second order reactions.
- Evaluation of proposed reaction mechanisms to be consistent with kinetic and stoichiometric data.

Guidance:

- Calculations will be limited to orders with whole number values.
- Consider concentration–time and rate–concentration graphs.
- Use potential energy level profiles to illustrate multi-step reactions; showing the higher E_a in the rate-determining step in the profile.
- Catalysts are involved in the rate-determining step.
- Reactions where the rate-determining step is not the first step should be considered.
- Any experiment which allows students to vary concentrations to see the effect upon the rate and hence determine a rate equation is appropriate.

16.2 Activation energy

Understandings:

- The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.
- A graph of $1/T$ against $\ln k$ is a linear plot with gradient $-E_a / R$ and intercept, $\ln A$.
- The frequency factor (or pre-exponential factor) (A) takes into account the frequency of collisions with proper orientations.

Applications and skills:

- Analysing graphical representation of the Arrhenius equation in its linear form.

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

- Using the Arrhenius equation:

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

- Describing the relationships between temperature and rate constant; frequency factor and complexity of molecules colliding.
- Determining and evaluating values of activation energy and frequency factors from data.
- Guidance:
- Use energy level diagrams to illustrate multi-step reactions showing the RDS in the diagram.
- Consider various data sources in using the linear expression:

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

- The expression below is given in the data booklet:

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

Rate expressions

- The rate expression or rate law for a reaction is an equation that includes the rate constant k and the concentration of the reactants (s) raised to a power.



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

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

Overall order of reaction is $x + y$

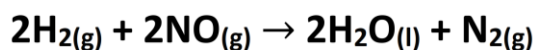
The rate constant k is a constant for a particular reaction at a **specified temperature**.

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

- The overall order for the reaction is the sum of the individual orders of reaction.

Orders of reaction and the rate expression can only be determined experimentally.

Example:



The above reaction was shown experimentally to be second order with respect to NO and first order with respect to H_2 . Write the rate expression below:

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

- The overall order of reaction is third order (add up the powers to which each concentration is raised).

Orders of reaction

- Orders of reaction can only be determined experimentally.

Zero order

- 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.

First order

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

Second order

- 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.

Summary:

| Change in concentration of reactant | Change in rate of zero-order reaction | Change in rate of first-order reaction | Change in rate of second-order reaction |
|-------------------------------------|---------------------------------------|--|---|
| Doubled ($\times 2$) | No change | $\times 2$ | $\times 4$ |
| Tripled ($\times 3$) | No change | $\times 3$ | $\times 9$ |
| Quadrupled ($\times 4$) | No change | $\times 4$ | $\times 16$ |

Units of rate constant k

- The rate constant k has different units, depending on the overall order of reaction.

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

Exercises:

1. Consider the reaction: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

The following data were obtained from three experiments using the method of initial rates:

| | Initial [NO] mol dm^{-3} | Initial [O ₂] mol dm^{-3} | Initial rate NO $\text{mol dm}^{-3}\text{s}^{-1}$ |
|--------------|--------------------------------------|---|--|
| 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} |

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant.
- Calculate the rate (in $\text{mol dm}^{-3}\text{s}^{-1}$) at the instant when $[\text{NO}] = 0.015 \text{ mol dm}^{-3}$ and $[\text{O}_2] = 0.0050 \text{ mol dm}^{-3}$

second order with respect to NO

first order with respect to O₂

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

From exp 1: $2.5 \times 10^{-5} = k(0.010)^2(0.010)$

$k = 25$

rate = $25 \times (0.015)^2 (0.0050)$

rate = $2.81 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

2. The reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ was studied at 904 °C, and the data in the table were collected.

| | Initial [NO] mol dm^{-3} | Initial [H ₂] mol dm^{-3} | Initial rate $\text{mol dm}^{-3}\text{s}^{-1}$ |
|--------------|--------------------------------------|---|---|
| Experiment 1 | 0.420 | 0.122 | 0.136 |
| Experiment 2 | 0.210 | 0.122 | 0.0339 |
| Experiment 3 | 0.210 | 0.244 | 0.0678 |
| Experiment 4 | 0.105 | 0.488 | 0.0339 |

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant at 904 °C.

second order with respect to NO

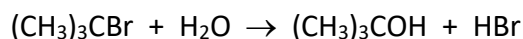
first order with respect to H₂

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

From exp 1: $0.136 = k(0.420)^2(0.122)$

$k = 6.3$

3. The reaction of butyl-bromide $(\text{CH}_3)_3\text{CBr}$ with water is represented by the equation:



The following data were obtained from three experiments using the method of initial rates:

| | Initial $[(\text{CH}_3)_3\text{CBr}]$ mol dm^{-3} | Initial $[\text{H}_2\text{O}]$ mol dm^{-3} | Initial rate $\text{mol dm}^{-3} \text{min}^{-1}$ |
|--------------|---|--|--|
| Experiment 1 | 5.0×10^{-2} | 2.0×10^{-2} | 2.0×10^{-6} |
| Experiment 2 | 5.0×10^{-2} | 4.0×10^{-2} | 2.0×10^{-6} |
| Experiment 3 | 1.0×10^{-1} | 4.0×10^{-2} | 4.0×10^{-6} |

- What is the order with respect to $(\text{CH}_3)_3\text{CBr}$?
- What is the order with respect to H_2O ?
- What is the overall order of the reaction?
- Write the rate equation.
- Calculate the rate constant, k , for the reaction.

First order with respect to $(\text{CH}_3)_3\text{CBr}$

Zero order with respect to H_2O

Overall order = 2nd order

rate = $k[(\text{CH}_3)_3\text{CBr}]$

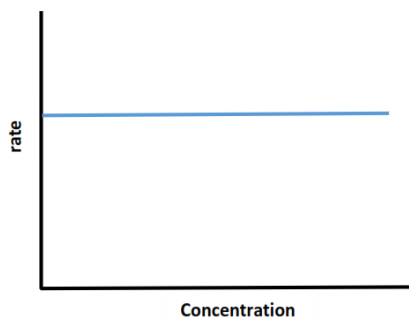
From exp 1: $2.0 \times 10^{-6} = k (5.0 \times 10^{-2})$

$k = 4 \times 10^{-5}$

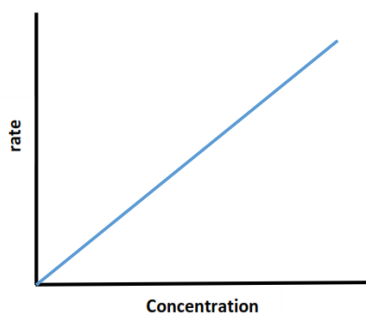
Graphical representations of reaction kinetics

Rate vs concentration

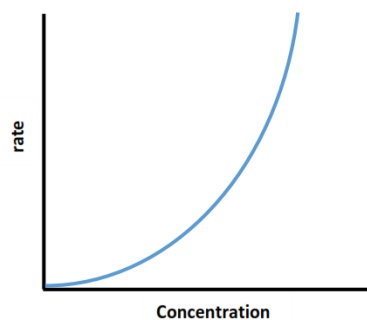
Zero order



First order

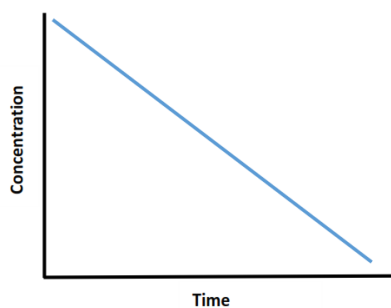


Second order

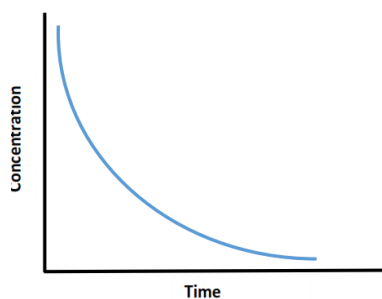


Concentration vs time

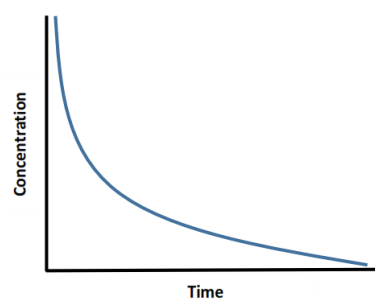
Zero order



First order



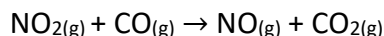
Second order



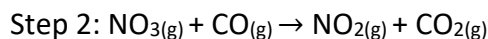
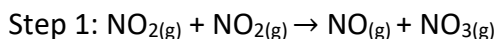
Reaction mechanism

- Most reactions occur in a series of simple steps.
- The sequence of steps is called the reaction mechanism.
- The individual steps, called elementary steps cannot be observed directly so the mechanism is a theory about the sequence from reactants to products.

For example, in the reaction:

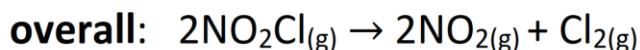
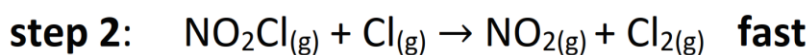
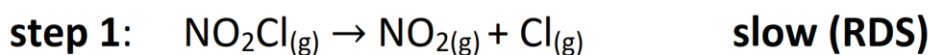


- It has been shown that the mechanism involves the following elementary steps:



- In this reaction, NO_3 is an intermediate - it is being produced and consumed in different steps so it doesn't appear in the overall equation.
- **The elementary steps must add up to the overall equation.**

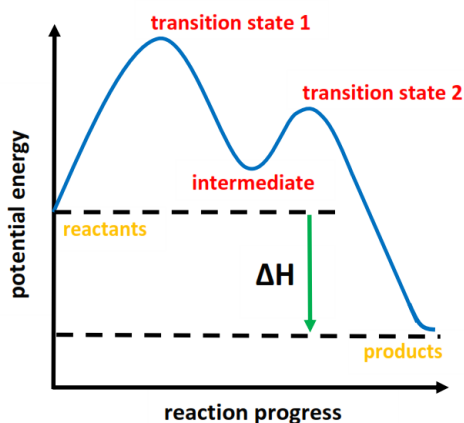
Example:



Is there an intermediate in the reaction? $\text{Cl}_{(g)}$ as it doesn't appear in the overall equation

Do the elementary steps add up to the overall equation for the reaction? **Yes.**

Transition state theory



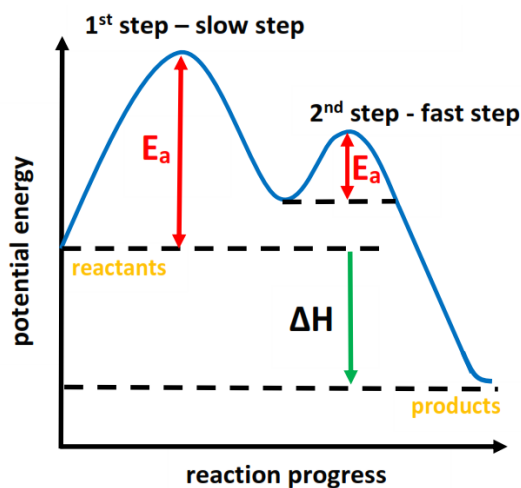
Transition state theory describes a hypothetical transition state that exists between reactants and products during a chemical reaction. The species formed in the transition state is called the activated complex.

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

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

Energy level profile for a two-step reaction:

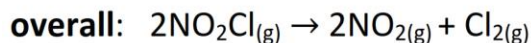
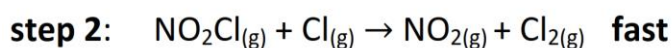
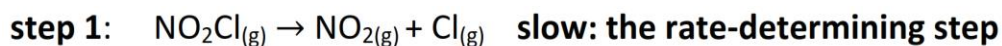


Which step has the highest activation energy? **Step 1**

Which step is the rate determining step? **Step 2 – it has the lowest activation energy.**

The rate expression is deduced from the slowest step (the rate-determining step).

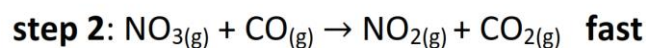
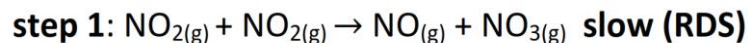
Exercise 1:



Write the rate expression:

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

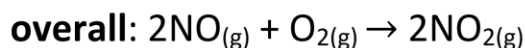
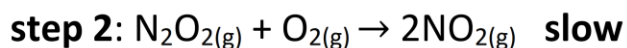
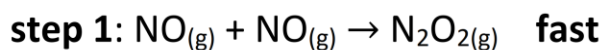
Exercise 2:



Write the rate expression:

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

Exercise 3:



Write the rate expression:

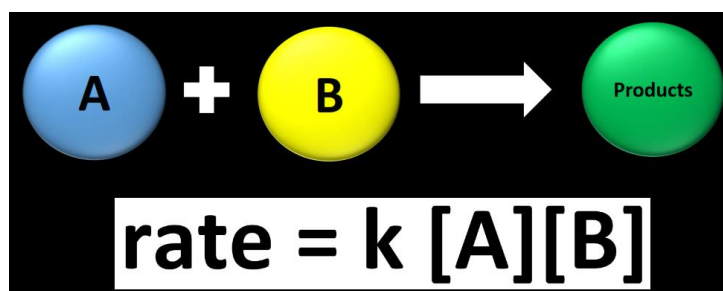
$\text{rate} = k[\text{NO}]^2[\text{O}_2]$

Molecularity

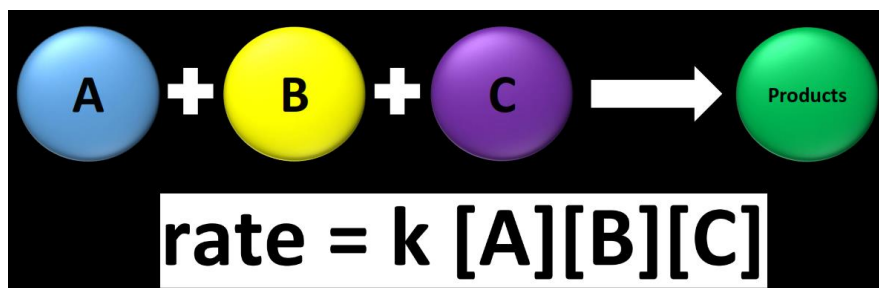
- The term molecularity indicates the number of reactant particles in the rate determining step.
- Unimolecular – a rate determining step that involves a single reactant particle.



- Bimolecular - a rate determining step with two reactant particles.



- Termolecular - a rate determining step with three reactant particles (very low probability).



Activation energy

The Arrhenius equation

- The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.
- The Arrhenius equation allows us to calculate the activation energy of a reaction.

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

A – Arrhenius constant (frequency factor)

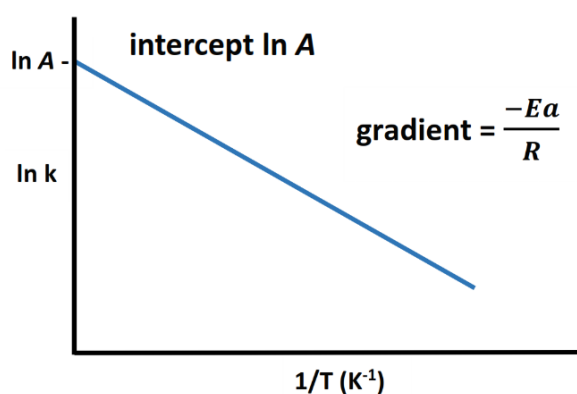
E_a – activation energy (J mol⁻¹)

R – gas constant (8.31 J K⁻¹ mol⁻¹)

- 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:

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

$$y = mx + c$$

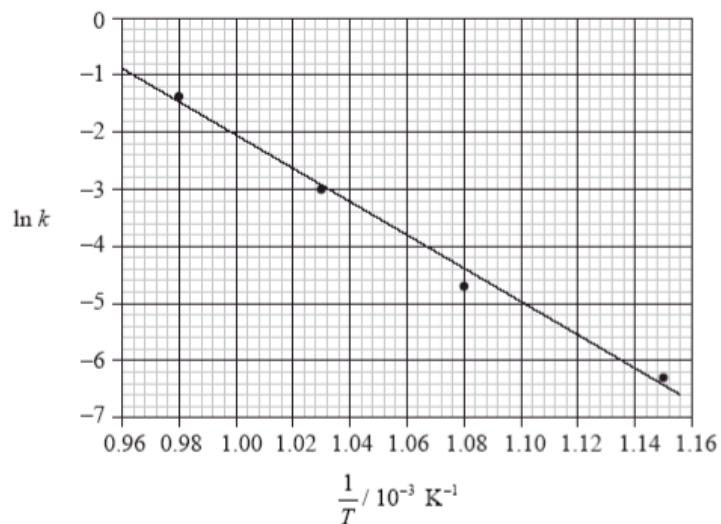


A graph of $\ln k$ (y-axis) against $1/T$ (x-axis) gives a straight line with the gradient $-E_a/R$

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

Example:

Calculate the activation energy from the graph below:



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

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

Allow value in range -28800 – 31300 (K)

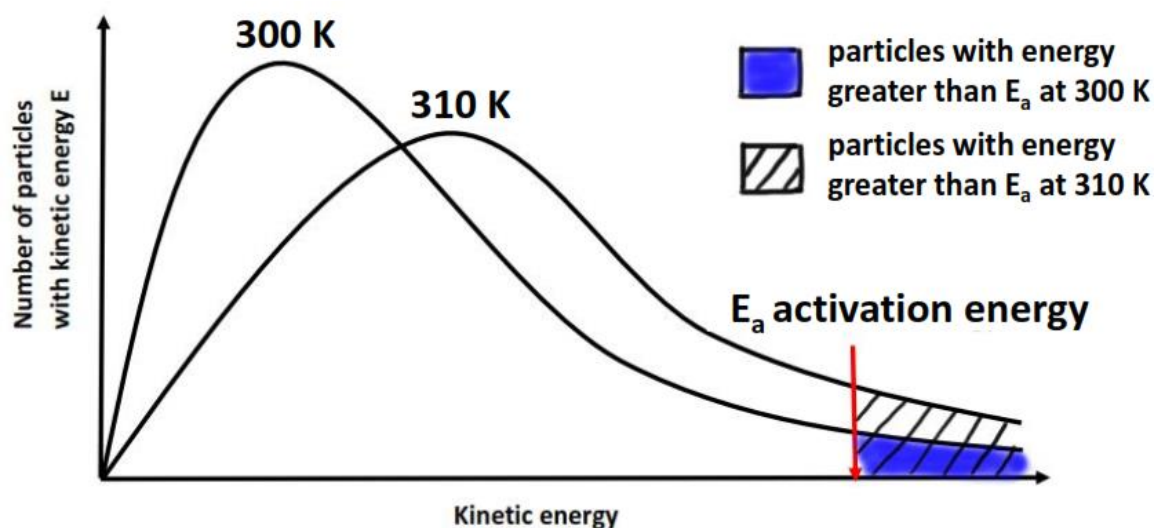
$$E_a = 30000 \times 8.31 = 2.49 \times 10^5 \text{ J mol}^{-1} / 249 \text{ kJ mol}^{-1}$$

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

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

Temperature and the rate constant k

- The Arrhenius equation can be used to show the effect of increasing the temperature on the rate constant k and therefore the rate of a reaction.



Exercise:

Explain why the rate of reaction increases with increased temperature.

At a higher temperature, a greater proportion of reactant particles have energy greater than the activation energy. This results in an increased frequency of collisions between reactant particles and an increase in the rate of reaction.

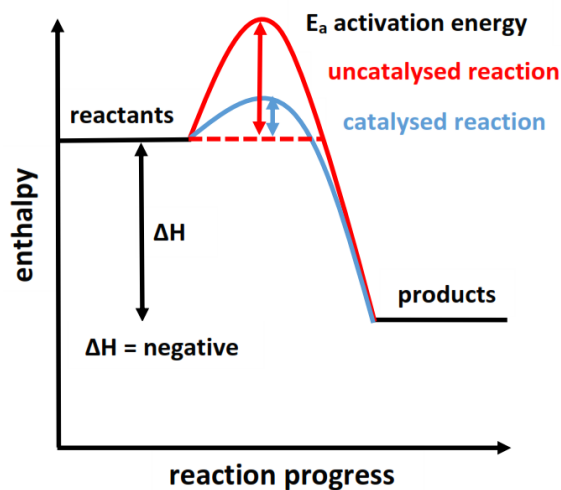
- For most reactions, an increase in temperature of 10 K (10°C) doubles the rate of reaction.
- In the Arrhenius equation $e^{(-E_a/RT)}$ is the fraction of molecules which have energy equal to or greater than activation energy at a particular temperature.

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

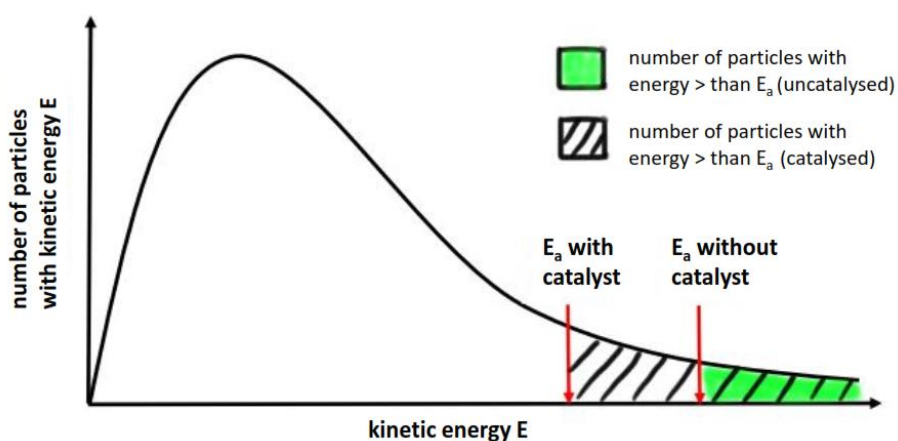
- The Arrhenius constant (A) is approximately constant for such a small increase in temperature (10 K).

Catalysts

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

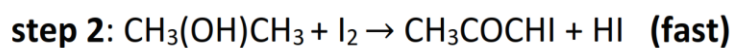
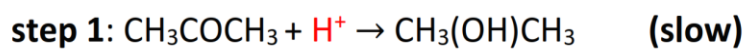
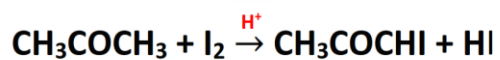


- Catalysts alter the reaction mechanism, introducing a step with lower activation energy.
- A catalyst is not consumed during the course of the reaction.



- At the same temperature, the catalysed reaction has a higher proportion 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 are involved in the rate determining step but do not appear in the overall equation.
- In the example below, the H^+ is the catalyst. It is shown in the rate expression but not in the overall equation.



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