

Kinetics HL

IB CHEMISTRY HL

<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>
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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 $x + y$

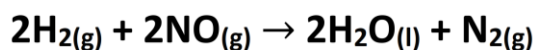
The rate constant k is a constant for a particular reaction at a **specified temperature**.

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 H₂. Write the rate expression below:

- 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 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: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

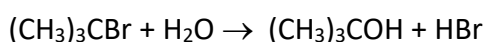
The following data were obtained from three experiments using the method of initial rates:

	Initial $[\text{NO}]$ mol dm^{-3}	Initial $[\text{O}_2]$ mol dm^{-3}	Initial rate $\text{mol dm}^{-3}\text{s}^{-1}$
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}

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

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

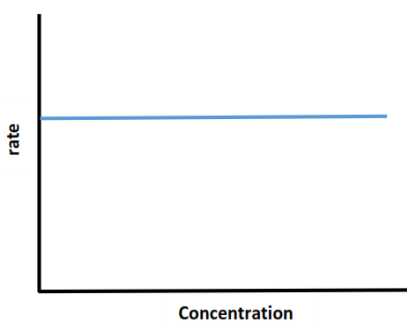
	Initial $[(\text{CH}_3)_3\text{CBr}]$ mol dm^{-3}	Initial $[\text{H}_2\text{O}]$ mol dm^{-3}	Initial rate $\text{mol dm}^{-3}\text{min}^{-1}$
Experiment 1	5.0×10^{-2}	2.0×10^{-2}	2.0×10^{-6}
Experiment 2	5.0×10^{-2}	4.0×10^{-2}	2.0×10^{-6}
Experiment 3	1.0×10^{-1}	4.0×10^{-2}	4.0×10^{-6}

- 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.

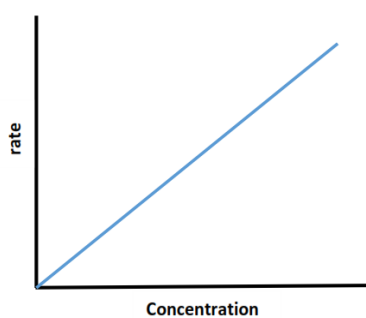
Graphical representations of reaction kinetics

Rate vs concentration

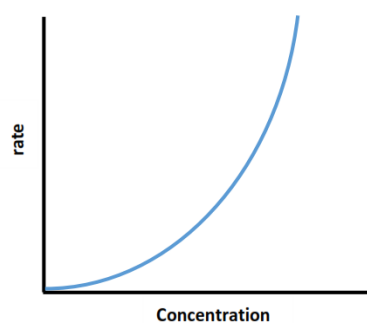
Zero order



First order

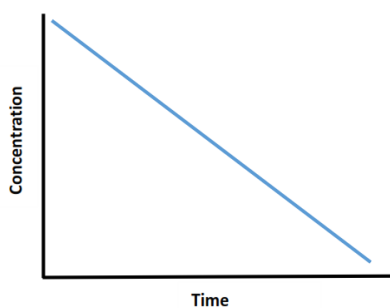


Second order

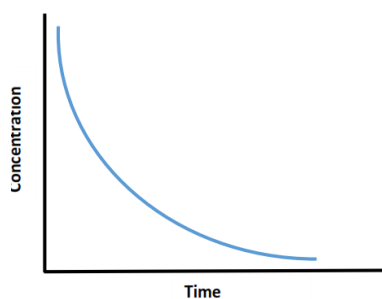


Concentration vs time

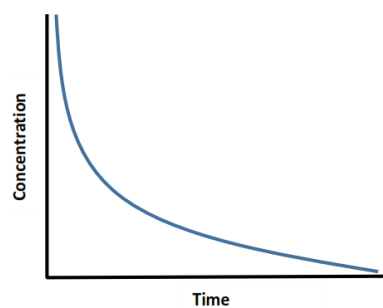
Zero order



First order



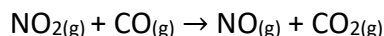
Second order



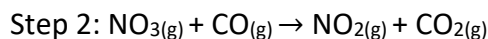
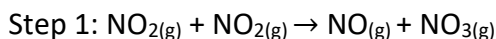
Reaction mechanism

- 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:

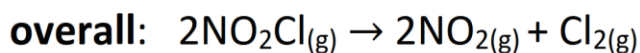
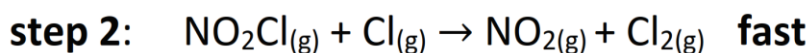
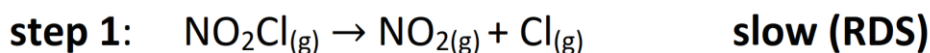


- It has been shown that the mechanism involves the following elementary steps:



- 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.**

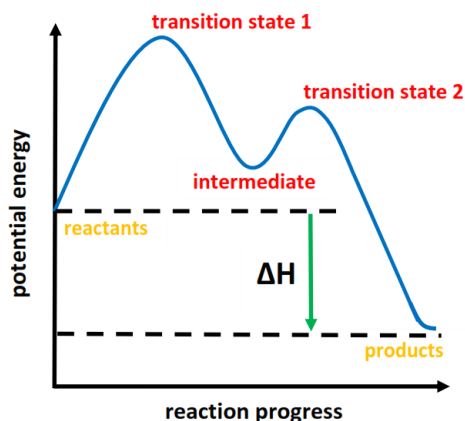
Example:



Is there an intermediate in the reaction?

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

Transition state theory



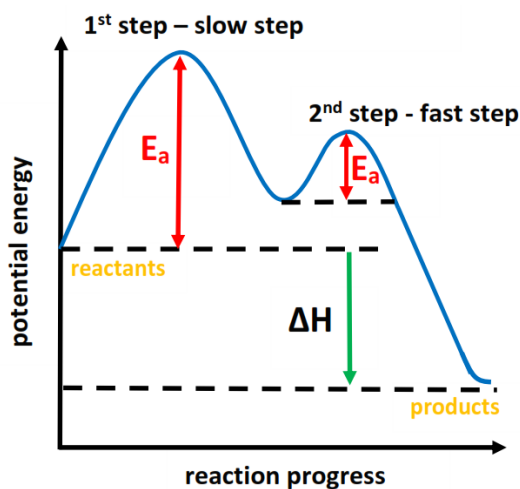
Transition state theory describes a hypothetical transition state that exists between reactants and products during a chemical reaction. The species formed in the transition state is called the activated complex.

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?

Which step is the rate determining step?

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

Exercise 1:

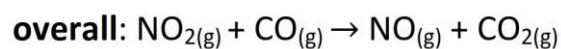
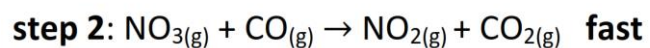
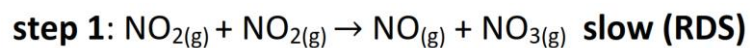
step 1: $\text{NO}_2\text{Cl}_{(\text{g})} \rightarrow \text{NO}_{2(\text{g})} + \text{Cl}_{(\text{g})}$ **slow: the rate-determining step**

step 2: $\text{NO}_2\text{Cl}_{(\text{g})} + \text{Cl}_{(\text{g})} \rightarrow \text{NO}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$ **fast**

overall: $2\text{NO}_2\text{Cl}_{(\text{g})} \rightarrow 2\text{NO}_{2(\text{g})} + \text{Cl}_{2(\text{g})}$

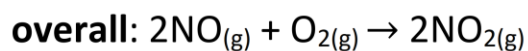
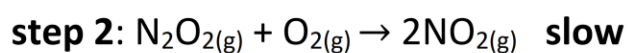
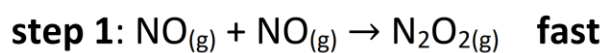
Write the rate expression:

Exercise 2:



Write the rate expression:

Exercise 3:



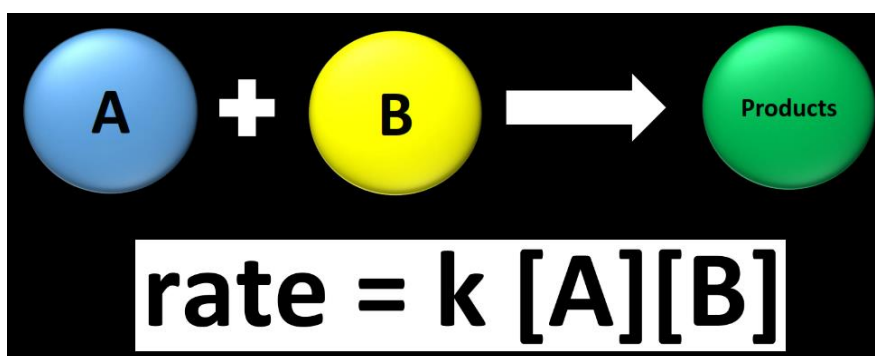
Write the rate expression:

Molecularity

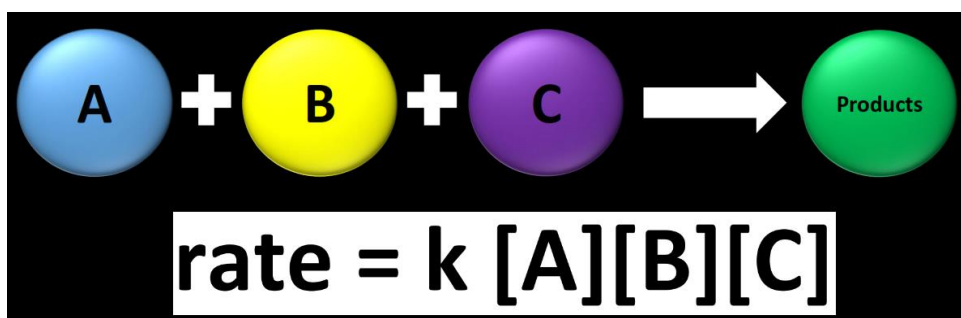
- The term molecularity indicates the number of reactant particles in the rate determining step.
- Unimolecular – a rate determining step that involves a single reactant particle.



- 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)

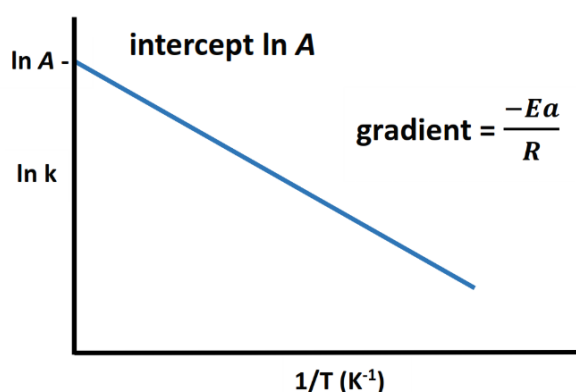
E_a – activation energy (J mol⁻¹)

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:

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

$$y = mx + c$$

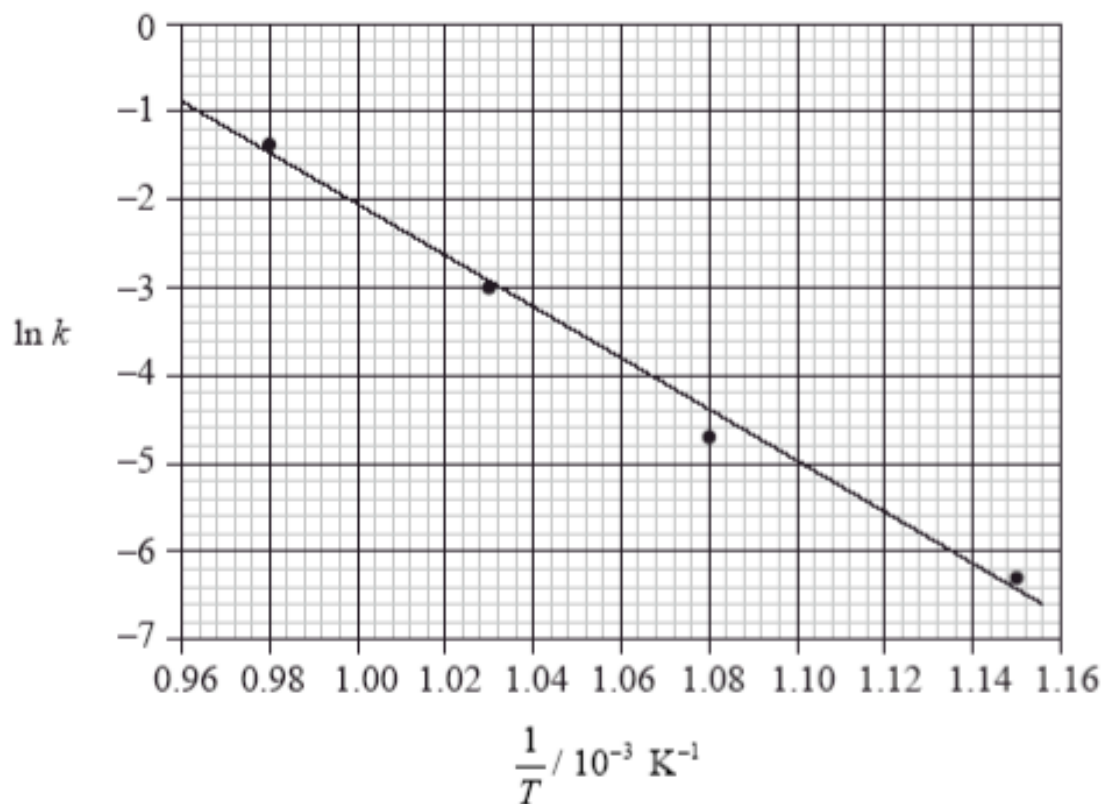


A graph of $\ln k$ (y-axis) against $1/T$ (x-axis) gives a straight line with the gradient $-E_a/R$

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

Example:

Calculate the activation energy from the graph below:

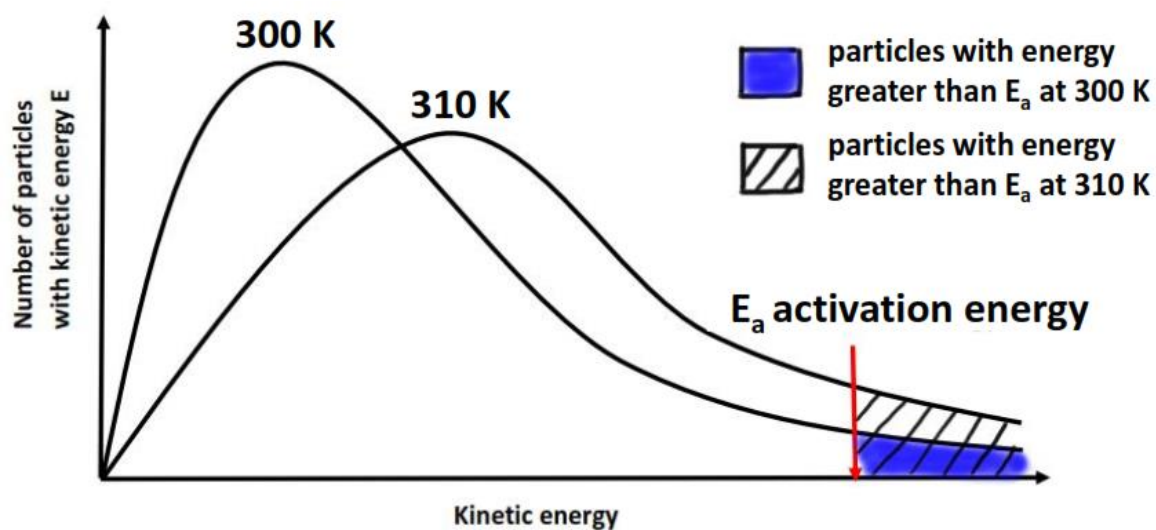


- The activation energy can also be calculated from values of the rate constant k at two different temperatures.

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

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.

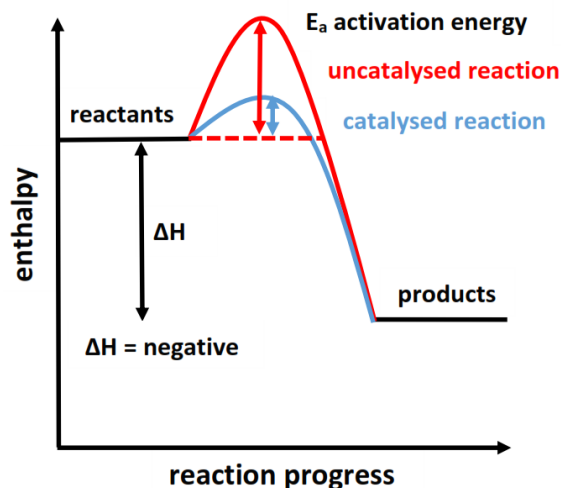
- For most reactions, an increase in temperature of 10 K (10°C) doubles the rate of reaction.
- In the Arrhenius equation $e^{(-E_a/RT)}$ is the fraction of molecules which have energy equal to or greater than activation energy at a particular temperature.

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

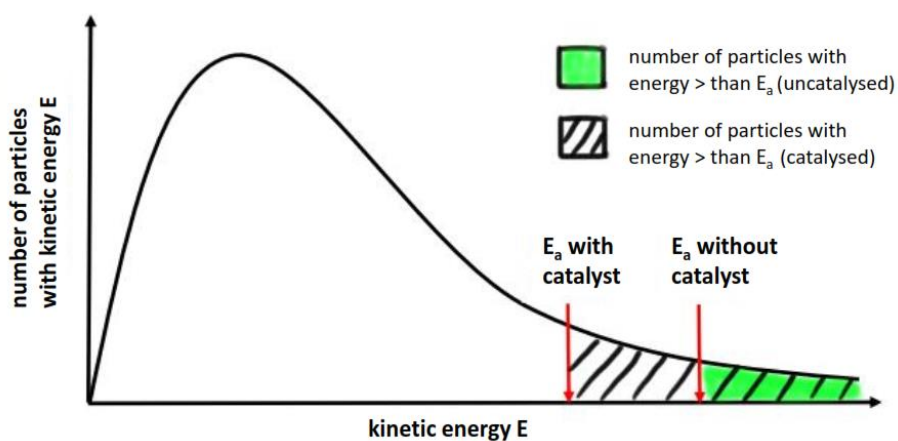
- The Arrhenius constant (A) is approximately constant for such a small increase in temperature (10 K).

Catalysts

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

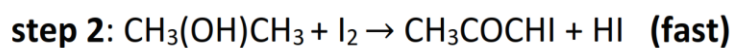
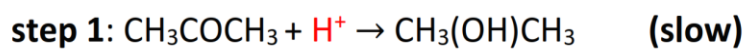
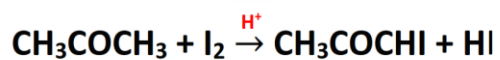


- Catalysts alter the reaction mechanism, introducing a step with lower activation energy.
- A catalyst is not consumed during the course of the reaction.



- 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.



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