

# Reactivity 2.2 HL

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IB CHEMISTRY HL

25 <b>Mn</b> Manganese 54.938045	16 <b>S</b> Sulfur 32.065	<b>J</b>	6 <b>C</b> Carbon 12.0107	2 <b>He</b> Helium 4.002602	25 <b>Mn</b> Manganese 54.938045
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## Reactivity 2.2.6

### Understandings:

- Many reactions occur in a series of elementary steps. The slowest step determines the rate of the reaction.

### Learning outcomes:

- Evaluate proposed reaction mechanisms and recognise intermediates.
- Distinguish between intermediates and transition states, and recognise both in energy profiles of reactions.

### Additional notes:

- Include examples where the rate-determining step is not the first step.
- Proposed reaction mechanisms must be consistent with kinetic and stoichiometric data.

### Linking questions:

- Reactivity 3.4 Which mechanism in the hydrolysis of halogenoalkanes involves an intermediate?

## Reactivity 2.2.7

### Understandings:

- Energy profiles can be used to show the activation energy and transition state of the rate-determining step in a multistep reaction.

### Learning outcomes:

- Construct and interpret energy profiles from kinetic data.

## Reaction mechanisms

- Chemical reactions can occur in a single step, known as elementary reactions, or in a series of steps, known as non-elementary reactions.
- The series of steps in a non-elementary reaction is known as the reaction mechanism.
- The individual steps that make up a reaction mechanism, called elementary steps, cannot be observed directly so the mechanism is only a theory about the sequence from reactants to products.
- Therefore, a reaction mechanism can never be proved, it can only be disproved.

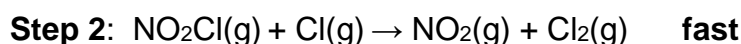
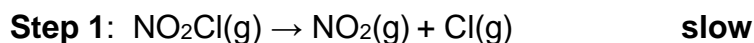
## Rate-determining step

- The rate-determining step is the slowest step in a reaction mechanism because it has the highest activation energy.
- The rate-determining step determines the overall rate of reaction.
- The rate equation is determined from the slowest step in the mechanism.

**Example:**  $\text{NO}_2\text{Cl}$  decomposes to form  $\text{NO}_2$  and  $\text{Cl}_2$ . The chemical equation for the reaction is shown.

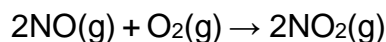


A proposed two-step mechanism is:

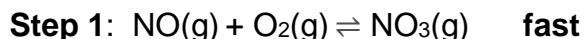


- The first step is the slow step, therefore, it is the rate-determining step.

**Exercise:** Nitrogen monoxide and oxygen react according to the equation shown:



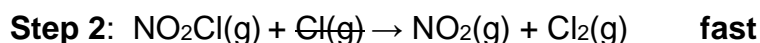
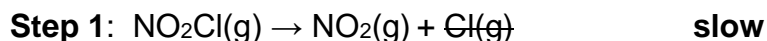
A proposed two-step mechanism is:



Which step is the rate-determining step? Which step has the highest activation energy?

## Reaction intermediates

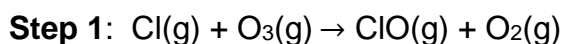
- Reaction intermediates are produced in one step and consumed in a subsequent step, therefore they do not appear in the overall equation for the reaction.
- In the mechanism shown below Cl(g) is a reaction intermediate because it is produced in one step and consumed in the next step.
- When the intermediates are crossed out the sum of the elementary steps must equal the overall equation.



## Catalysts and reaction mechanisms

- Catalysts are not consumed in the reaction so they appear in the reactant side of the first step and the product side of the last step.

**Example:** Consider the following reaction mechanism:



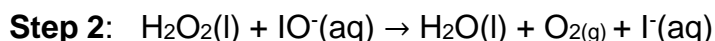
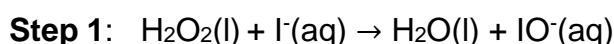
(a) Identify the intermediate in the mechanism.

(b) Identify the catalyst in the reaction.

(c) Write the overall equation for the reaction.

## Exercises:

1. Identify the intermediate and the catalyst in the following reaction mechanism. Then write the overall equation for the reaction.

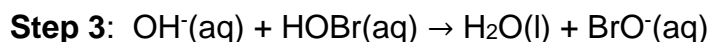
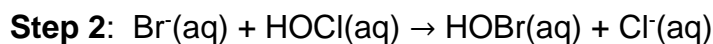
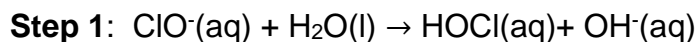


Intermediate:

Catalyst:

Overall equation:

2. Identify the intermediate and the catalyst in the following reaction mechanism. Then write the overall equation for the reaction.



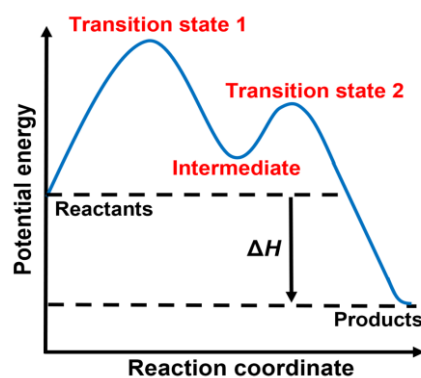
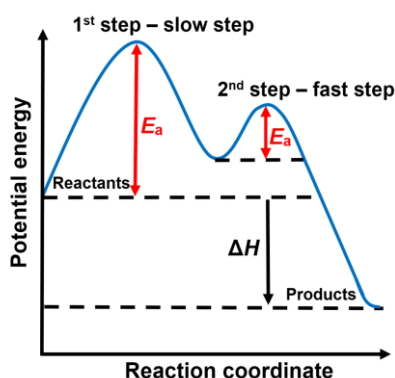
Intermediate:

Catalyst:

Overall equation:

### Energy level profiles for multi-step reactions

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



### Transition states and reaction intermediates

- 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 species in multi-step reactions which are produced and consumed in the elementary steps and do not appear in the overall chemical equation.
- The location of transition states and reaction intermediates in a two-step reaction are shown above.

## Reactivity 2.2.8

### Understandings:

- The molecularity of an elementary step is the number of reacting particles taking part in that step.

### Learning outcomes:

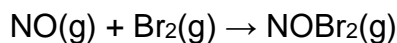
- Interpret the terms “unimolecular”, “bimolecular” and “termolecular”.

### Molecularity

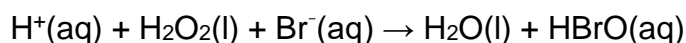
- The term molecularity indicates the number of reactant particles in an elementary step.
- An elementary step can be unimolecular, bimolecular or termolecular.
- A unimolecular elementary step involves a single reactant particle.
- Example:



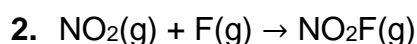
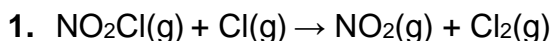
- A bimolecular elementary step involves two reactant particles.  
Example:



- A termolecular elementary step involves three reactant particles.
- Note that this has a low probability of occurring because of the requirements for three reactant particles to collide with sufficient energy and the correct orientation.  
Example:



**Exercise:** Determine the molecularity of the following elementary steps.



### Reactivity 2.2.9

#### Understandings:

- Rate equations depend on the mechanism of the reaction and can only be determined experimentally.

#### Learning outcomes:

- Deduce the rate equation for a reaction from experimental data.

### Reactivity 2.2.10

#### Understandings:

- The order of a reaction with respect to a reactant is the exponent to which the concentration of the reactant is raised in the rate equation.
- The order with respect to a reactant can describe the number of particles taking part in the rate-determining step.
- The overall reaction order is the sum of the orders with respect to each reactant.

#### Learning outcomes:

- Sketch, identify and analyse graphical representations of zero, first and second order reactions.

#### Additional notes:

- Concentration–time and rate–concentration graphs should be included.
- Only integer values for order of reaction will be assessed.

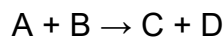
#### Linking questions:

- Tool 1, 3, Inquiry 2 What measurements are needed to deduce the order of reaction for a specific reactant?
- Nature of science Why are reaction mechanisms only considered as “possible mechanisms”?

## Rate equations

- The rate equation (or rate expression/rate law) for a reaction is an equation that includes the rate constant  $k$  and the concentration of the reactant(s) raised to a power.
- For an elementary reaction, the rate expression can be deduced from the balanced equation.

Example: the following is an elementary reaction (occurs in only one step):



- The rate equation can be deduced from the balanced equation:

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

- $k$  is the rate constant. It is a constant for a particular reaction at a specified temperature (it is temperature-dependent).
- $x$  and  $y$  are the orders of reaction (or partial orders of reaction) with respect to the reactants A and B.
- The sum of  $x+y$  is the overall reaction order.
- For non-elementary reactions, the rate equation cannot be deduced from the balanced chemical equation, instead, we must use experimental data to determine the rate equation.

## Orders of reaction

- Orders of reaction are the powers to which a reactant concentration is raised in the rate equation.
- Orders of reaction can only be determined from experimental data.
- Orders of reaction can be zero-order, first-order, or second-order.

### 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.

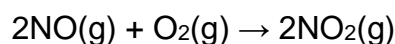
Change in concentration of reactant	Change in rate of zero-order reaction	Change in rate of first-order reaction	Change in rate of second-order reaction
Doubled ( $\times 2$ )	No change	$\times 2$	$\times 4$
Tripled ( $\times 3$ )	No change	$\times 3$	$\times 9$
Quadrupled ( $\times 4$ )	No change	$\times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



## Determining orders of reaction from experimental data

- Orders of reaction are determined from experimental data, known as the initial rates method.

**Example 1:** Nitrogen monoxide reacts with oxygen according to the equation shown. The following data was obtained from three experiments using the initial rates method for the reaction shown.



The following data was obtained from three experiments using the initial rates method for the reaction shown. Determine the orders of reaction with respect to each reactant.

	Initial [NO] mol dm <sup>-3</sup>	Initial [O <sub>2</sub> ] mol dm <sup>-3</sup>	Initial rate mol dm <sup>-3</sup> s <sup>-1</sup>
<b>Experiment 1</b>	0.010	0.010	2.5 × 10 <sup>-5</sup>
<b>Experiment 2</b>	0.020	0.010	1.0 × 10 <sup>-4</sup>
<b>Experiment 3</b>	0.010	0.020	5.0 × 10 <sup>-5</sup>

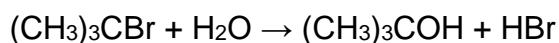
- In experiments 1 and 2, the concentration of NO is doubled. The concentration of O<sub>2</sub> is kept constant. The initial rate of reaction increases by a factor of 4. The rate of reaction increased by the square of the change (2<sup>2</sup> = 4) so the reaction is second-order with respect to NO.
- In experiments 1 and 3 the concentration of O<sub>2</sub> is doubled and the concentration of NO is kept constant. The initial rate of reaction doubles so the reaction is first-order with respect to O<sub>2</sub>.
- Now that the orders of reaction with respect to each reactant are known, the rate equation can be determined:

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

- The overall order of reaction is the sum of the individual orders of reaction (2+1=3) so the reaction is third-order overall.

### Exercises:

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

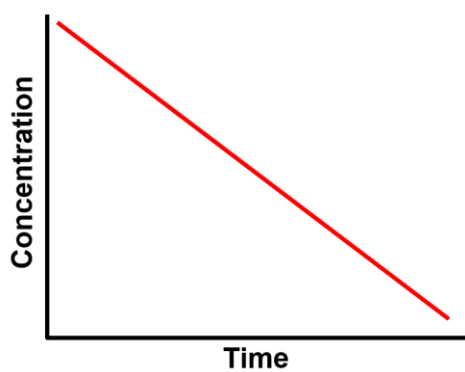
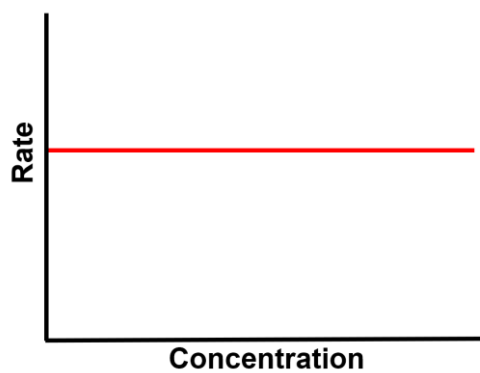
- (a) Determine the order of reaction with respect to each reactant.
- (b) Determine the rate equation for the reaction and the overall order.
- (c) Calculate the value of the rate constant,  $k$ .
2. The reaction:  $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$  was studied at  $904^\circ\text{C}$ , and the data in the table was collected.

	Initial $[\text{NO}]$ $\text{mol dm}^{-3}$	Initial $[\text{H}_2]$ $\text{mol dm}^{-3}$	Initial rate $\text{mol dm}^{-3} \text{s}^{-1}$
<b>Experiment 1</b>	0.420	0.122	0.136
<b>Experiment 2</b>	0.210	0.122	0.0339
<b>Experiment 3</b>	0.210	0.244	0.0678
<b>Experiment 4</b>	0.105	0.488	0.0339

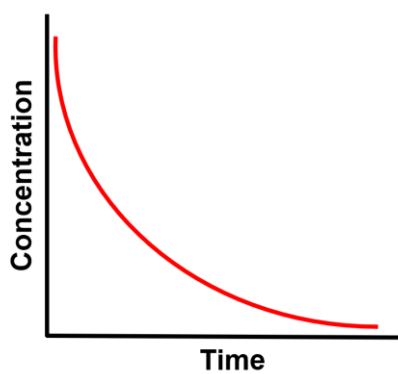
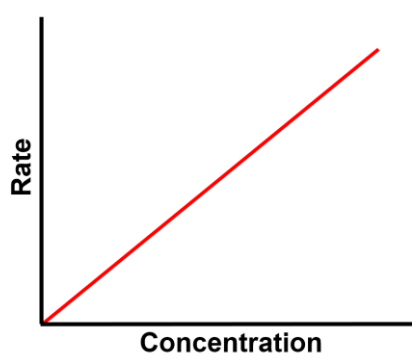
- (a) Determine the order of the reaction with respect to each reactant.
- (b) Write the rate equation for the reaction and the overall order.
- (c) Calculate the value of the rate constant,  $k$ .

## Graphical representations of reaction kinetics

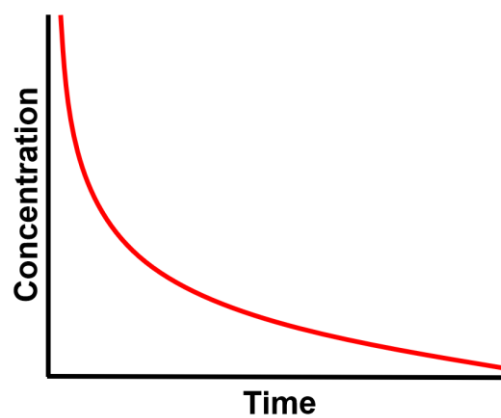
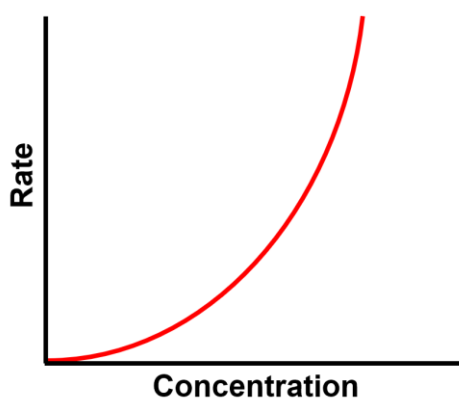
Zero-order



First-order



Second-order



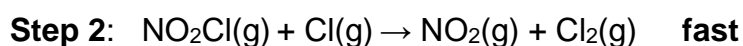
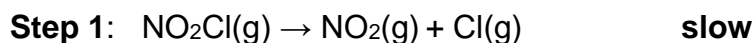
### Determine the rate equation from the reaction mechanism

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

**Example 1:**  $\text{NO}_2\text{Cl}$  decomposes to form  $\text{NO}_2$  and  $\text{Cl}_2$ . The chemical equation for the reaction is shown.



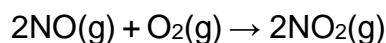
A proposed two-step mechanism is:



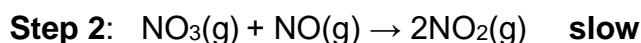
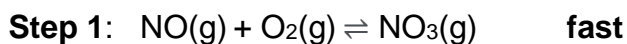
The rate equation is determined from the slow step, therefore:

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

**Example 2:** Nitrogen monoxide and oxygen react according to the equation shown:



A proposed two-step mechanism is:



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

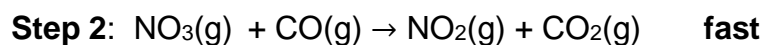
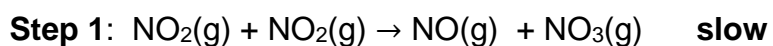
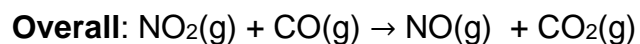
In this mechanism,  $\text{NO}_3$  is an intermediate and cannot be included in the rate equation. The concentration of the intermediate depends on the  $[\text{NO}]$  and  $[\text{O}_2]$  in step 1 so the rate equation is:

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

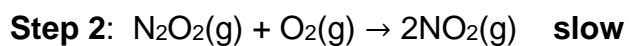
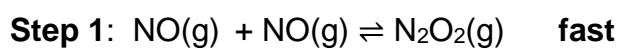
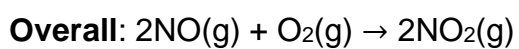
Note that we include the  $[\text{NO}]$  in the second step in the rate equation.

**Exercise:** Write the rate equations for the following.

1. Consider the following reaction and proposed reaction mechanism:



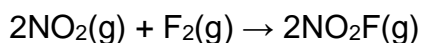
2. Consider the following reaction and proposed reaction mechanism:



## Evaluate a reaction mechanism from experimental data

- 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.

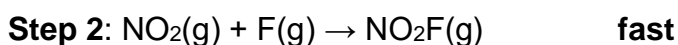
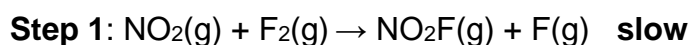
**Example:** Consider the reaction:



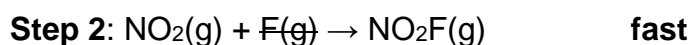
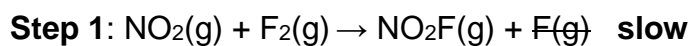
- The rate equation determined from experimental data is:

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

- The proposed two-step reaction mechanism is:



Do the elementary steps add up to the overall equation?



Yes, when the intermediate, F(g), is canceled out.

Is the rate equation determined from the slow step consistent with the rate equation determined from the experimental data?

The rate equation determined from the slow step is:

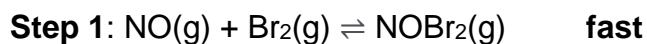
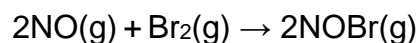
$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$

This is consistent with the experimental data - the reaction is first-order with respect to NO<sub>2</sub> and F<sub>2</sub>.

- Based on these two points, this is a possible mechanism for the reaction.

## Exercises

1. Consider the reaction and proposed reaction mechanism.



The rate equation determined from experimental data is:

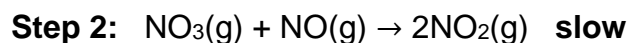
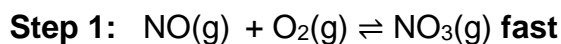
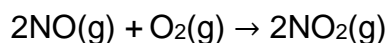
$$\text{rate} = k[\text{NO}]^2[\text{Br}_2]$$

Do the elementary steps add up to the overall equation?

Is the rate equation determined from the slow step consistent with the rate equation determined from the experimental data?

Is this a possible reaction mechanism for the reaction?

2. Consider the reaction and a proposed reaction mechanism.



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). Is this a possible reaction mechanism for the reaction?

## Reactivity 2.2.11

### Understandings:

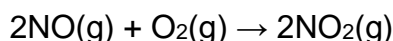
- The rate constant,  $k$ , is temperature dependent and its units are determined from the overall order of the reaction.

### Learning outcomes:

- Solve problems involving the rate equation, including the units of  $k$ .

### Calculate the value of the rate constant $k$

- In the previous section, the orders of reaction with respect to each reactant were determined together with the rate equation for the reaction shown.



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

- Next, we will calculate the value of the rate constant  $k$  using the rate equation and data from the table below.

	Initial [NO] mol dm <sup>-3</sup>	Initial [O <sub>2</sub> ] mol dm <sup>-3</sup>	Initial rate mol dm <sup>-3</sup> s <sup>-1</sup>
Experiment 1	0.010	0.010	2.5 × 10 <sup>-5</sup>
Experiment 2	0.020	0.010	1.0 × 10 <sup>-4</sup>
Experiment 3	0.010	0.020	5.0 × 10 <sup>-5</sup>

Using the data from experiment 1:

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

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

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

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

- Note that because all experiments were assumed to be carried out at the same temperature, the value of the rate constant will be the same regardless of which experimental data is used.



### 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
$\text{mol dm}^{-3} \text{s}^{-1}$	$\text{s}^{-1}$	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

- In the above example, the overall order of reaction was third order, so the units are  $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

### Reactivity 2.2.12

#### Understandings:

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

#### Learning outcomes:

- Describe the qualitative relationship between temperature and the rate constant.
- Analyse graphical representations of the Arrhenius equation, including its linear form.

#### Additional notes:

- The Arrhenius equation and its linear form are given in the data booklet.
- Linking questions:
- Reactivity 3.4 What are the rate equations and units of  $k$  for the reactions of primary and tertiary halogenoalkanes with aqueous alkali?

### Reactivity 2.2.13

#### Understandings:

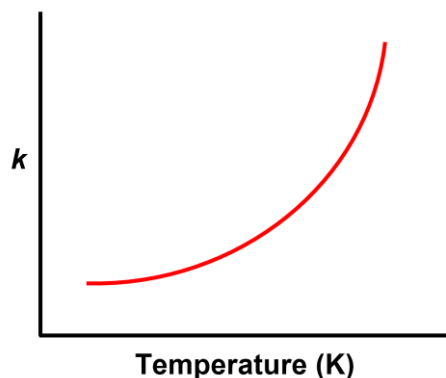
- The Arrhenius factor,  $A$ , takes into account the frequency of collisions with proper orientations.

#### Learning outcomes:

- Determine the activation energy and the Arrhenius factor from experimental data.

### Temperature dependence of the 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.



### The Arrhenius equation

- The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.
- The Arrhenius equation is shown below and can be found in section 1 of the IB data booklet.

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

$A$  is the Arrhenius constant (or frequency factor)

$e$  is Euler's number

$E_a$  is activation energy in  $\text{J mol}^{-1}$

$R$  is the universal gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$T$  is the temperature in  $\text{K}$

- The Arrhenius constant (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:

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

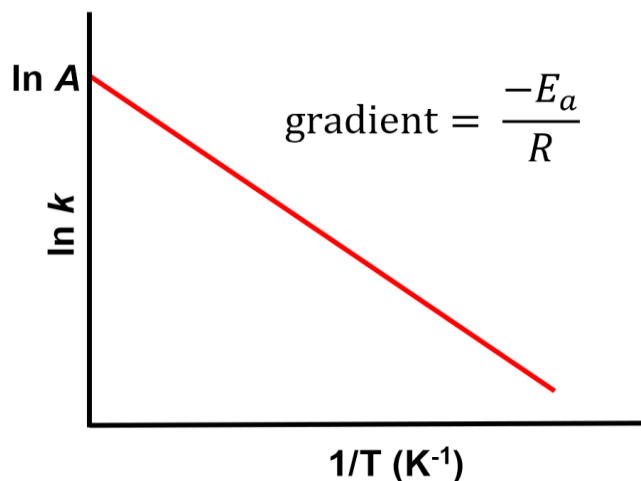
- This takes the form of the equation for a straight line:

$$y = mx + c$$

where  $m$  is the gradient, and  $c$  is the  $y$ -intercept ( $\ln A$ ).

### Determine the activation energy for a reaction graphically

- To determine the activation energy for a reaction, the reaction is carried out at different temperatures and the value of the rate constant is calculated for each temperature.
- A graph of  $\ln k$  against  $1/T$  gives a straight line with the gradient  $-E_a/R$ .
- The intercept of the y-axis is the natural log of the Arrhenius constant,  $\ln A$ .



- The activation energy in  $\text{J mol}^{-1}$  can be calculated using the equation:

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

**Exercise:** Calculate the activation energy, in  $\text{kJ mol}^{-1}$ , from the graph below.

