

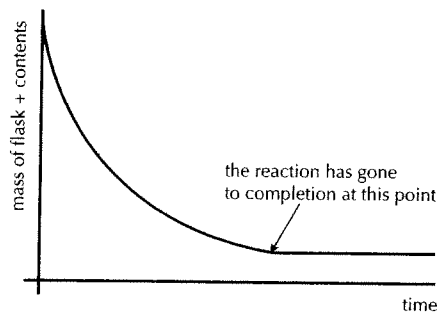
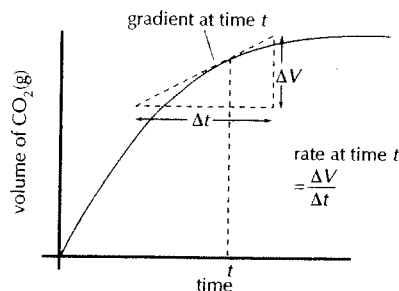
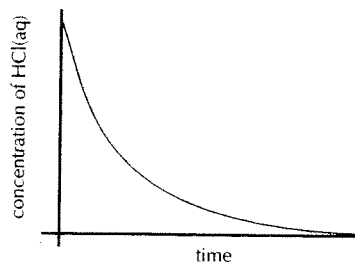
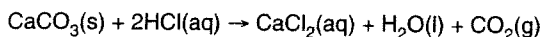
Rates of reaction and collision theory

RATE OF REACTION

Chemical kinetics is the study of the factors affecting the rate of a chemical reaction. The rate of a chemical reaction can be defined either as the increase in the concentration of one of the products per unit time or as the decrease in the concentration of one of the reactants per unit time. It is measured in $\text{mol dm}^{-3} \text{ s}^{-1}$.

The change in concentration can be measured by using any property that differs between the reactants and the products. Common methods include mass or volume changes when a gas is evolved, absorption using a spectrometer when there is a colour change, pH changes when there is a change in acidity, and electrical conductivity when there is a change in the ionic concentrations. Data loggers could be used for all these methods. A graph of concentration against time is then usually plotted. The rate at any stated point in time is then the gradient of the graph at that time. Rates of reaction usually decrease with time as the reactants are used up.

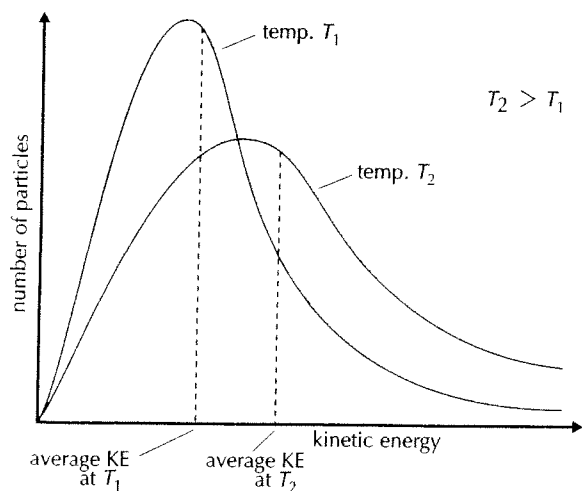
The reaction of hydrochloric acid with calcium carbonate can be used to illustrate three typical curves that could be obtained depending on whether the concentration of reactant, the volume of the product or the loss in mass due to the carbon dioxide escaping is followed.



MAXWELL-BOLTZMANN DISTRIBUTION

The moving particles in a gas or liquid do not all travel with the same velocity. Some are moving very fast and others much slower. The faster they move the more kinetic energy they possess. The distribution of kinetic energies is shown by a Maxwell-Boltzmann curve.

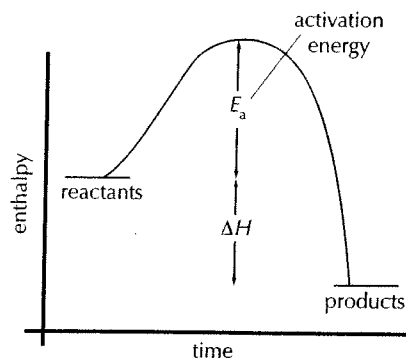
As the temperature increases the area under the curve does not change as the total number of particles remains constant. More particles have a very high velocity resulting in an increase in the average kinetic energy, which leads to a broadening of the curve.



COLLISION THEORY

For a reaction between two particles to occur three conditions must be met.

- The particles must collide.
- They must collide with the appropriate geometry or orientation so that the reactive parts of the particles come into contact with each other.
- They must collide with sufficient energy to bring about the reaction.

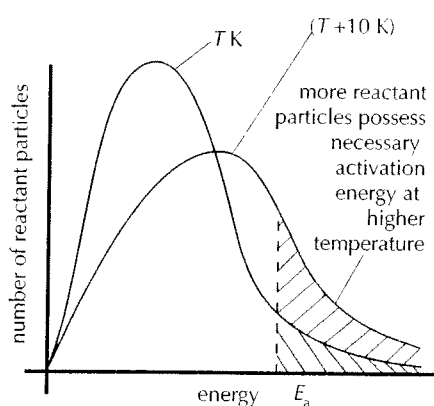
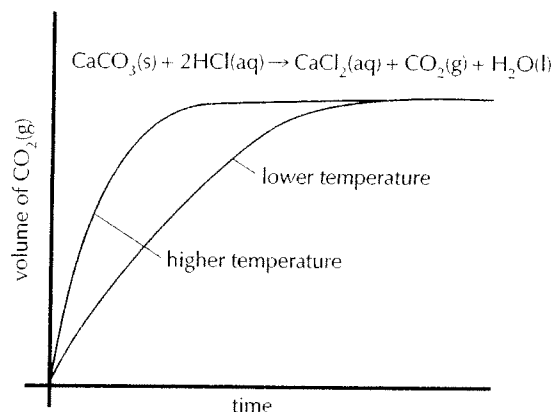


This minimum amount of energy required is known as the **activation energy**. Any factor that either increases the frequency of the collisions or increases the energy with which they collide will make the reaction go faster.

Factors affecting the rate of reaction

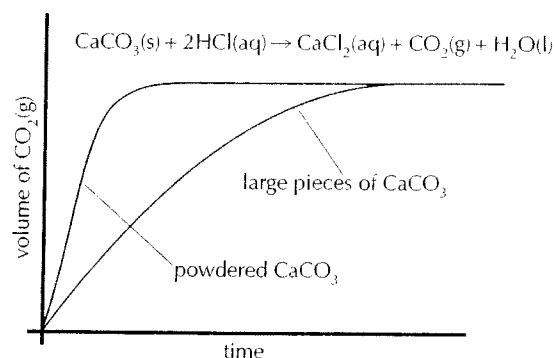
TEMPERATURE

As the temperature increases the particles will move faster so there will be more collisions per second. However, the main reason why an increase in temperature increases the rate is that more of the colliding particles will possess the necessary activation energy resulting in more successful collisions. As a rough rule of thumb an increase of 10 °C doubles the rate of a chemical reaction.



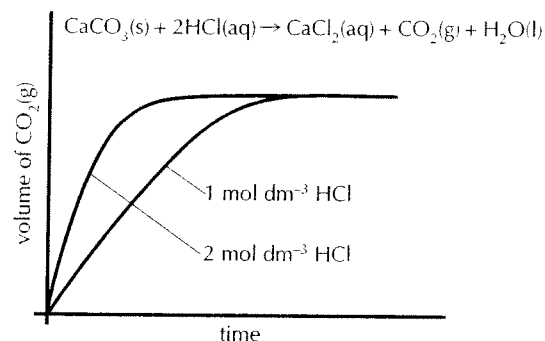
SURFACE AREA

In a solid substance only the particles on the surface can come into contact with a surrounding reactant. If the solid is in powdered form then the surface area increases dramatically and the rate increases correspondingly.



CONCENTRATION

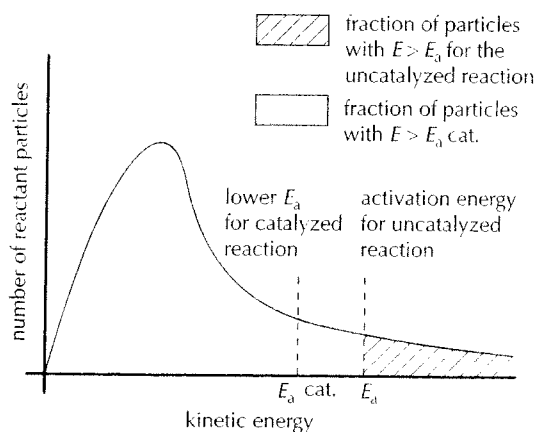
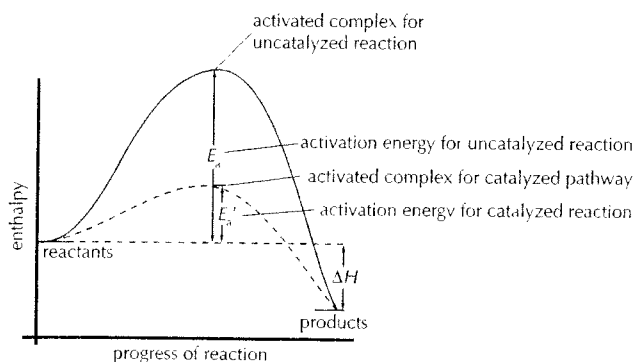
The more concentrated the reactants the more collisions there will be per second per unit volume. As the reactants get used up their concentration decreases. This explains why the rate of most reactions gets slower as the reaction proceeds. (Some exothermic reactions do initially speed up if the heat that is given out more than compensates for the decrease in concentration.)



Note: this graph assumes that calcium carbonate is the limiting reagent or that equal amounts (mol) of acid have been added.

CATALYST

Catalysts increase the rate of a chemical reaction without themselves being chemically changed at the end of the reaction. They work essentially by bringing the reactive parts of the reactant particles into close contact with each other. This provides an alternative pathway for the reaction with a lower activation energy. More of the reactants will possess this lower activation energy, so the rate increases.





Order of reaction and half-life

RATE EXPRESSIONS

The rate of reaction between two reactants, A and B, can be followed experimentally. The rate will be found to be proportional to the concentration of A raised to some power and also to the concentration of B raised to a power. If square brackets are used to denote concentration this can be written as $\text{rate} \propto [A]^x$ and $\text{rate} \propto [B]^y$. They can be combined to give the rate expression:

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

where k is the constant of proportionality and is known as the **rate constant**.

x is known as the **order of the reaction** with respect to A.

y is known as the order of the reaction with respect to B.

The overall order of the reaction = $x + y$.

Note: the order of the reaction and the rate expression can only be determined experimentally. They cannot be deduced from the balanced equation for the reaction.

UNITS OF RATE CONSTANT

The units of the rate constant depend on the overall order of the reaction.

First order: $\text{rate} = k[A]$

$$k = \frac{\text{rate}}{[A]} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$$

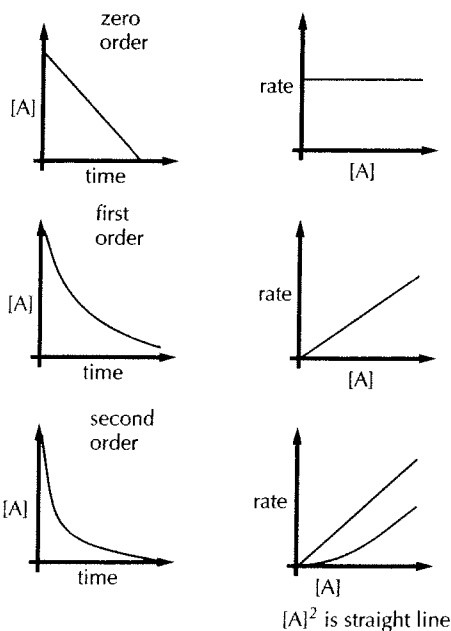
Second order: $\text{rate} = k[A]^2$ or $k = [A][B]$

$$k = \frac{\text{rate}}{[A]^2} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Third order: $\text{rate} = k[A]^2[B]$ or $\text{rate} = k[A][B]^2$

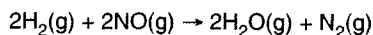
$$k = \frac{\text{rate}}{[A]^2[B]} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^3} = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

GRAPHICAL REPRESENTATIONS OF REACTIONS



DERIVING A RATE EXPRESSION BY INSPECTION OF DATA

Experimental data obtained from the reaction between hydrogen and nitrogen monoxide at 1073 K:



Experiment	Initial concentration of $\text{H}_2(\text{g})$ / mol dm^{-3}	Initial concentration of $\text{NO}(\text{g})$ / mol dm^{-3}	Initial rate of formation of $\text{N}_2(\text{g})$ / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	1×10^{-3}	6×10^{-3}	3×10^{-3}
2	2×10^{-3}	6×10^{-3}	6×10^{-3}
3	6×10^{-3}	1×10^{-3}	0.5×10^{-3}
4	6×10^{-3}	2×10^{-3}	2.0×10^{-3}

From experiments 1 and 2 doubling $[\text{H}_2]$ doubles the rate so $\text{rate} \propto [\text{H}_2]$.

From experiments 3 and 4 doubling $[\text{NO}]$ quadruples the rate so $\text{rate} \propto [\text{NO}]^2$.

Rate expression given by $\text{rate} = k[\text{H}_2][\text{NO}]^2$.

The rate is first order with respect to hydrogen, second order with respect to nitrogen monoxide, and third order overall. The value of k can be found by substituting the values from any one of the four experiments:

$$k = \frac{\text{rate}}{[\text{H}_2][\text{NO}]^2} = 8.33 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

HALF-LIFE $t_{1/2}$

For a first order reaction the rate of change of concentration of A is equal to $k[A]$. This can be expressed as $\frac{d[A]}{dt} = k[A]$.

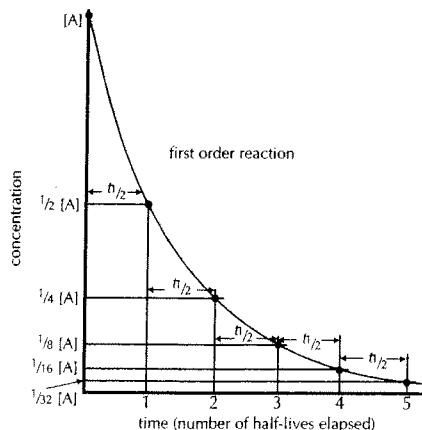
If this expression is integrated then $kt = \ln [A]_0 - \ln [A]$ where $[A]_0$ is the initial concentration and $[A]$ is the concentration at time t . This expression is known as the integrated form of the rate equation.

The half-life is defined as the time taken for the concentration of a reactant to fall to half of its initial value.

At $t_{1/2}$ $[A] = \frac{1}{2}[A]_0$ the integrated rate expression then becomes

$$kt_{1/2} = \ln [A]_0 - \ln \frac{1}{2}[A]_0 = \ln 2 \quad \text{since } \ln 2 = 0.693 \text{ this simplifies to } t_{1/2} = \frac{0.693}{k}$$

From this expression it can be seen that the half-life of a first order reaction is independent of the original concentration of A, i.e. first order reactions have a constant half-life.



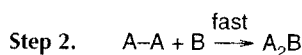
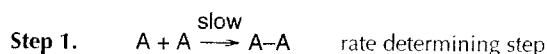


Reaction mechanisms and activation energy

REACTION MECHANISMS

Many reactions do not go in one step. This is particularly true when there are more than two reactant molecules as the chances of a successful collision between three or more particles is extremely small. When there is more than one step then each step will proceed at its own rate. No matter how fast the other steps are the overall rate of the reaction will depend only upon the rate of the slowest step. This slowest step is known as the **rate determining step**.

e.g. consider the reaction between A and B to form A_2B : $2A + B \rightarrow A_2B$. A possible mechanism might be:



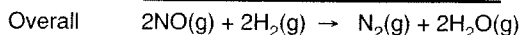
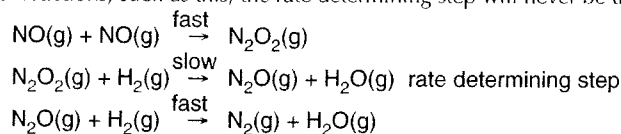
However fast A-A reacts with B the rate of production of A_2B will only depend on how fast A-A is formed.

When the separate steps in a chemical reaction are analysed there are essentially only two types of processes. Either a single species can break down into two or more products by what is known as a **unimolecular process**, or two species can collide and interact by a **bimolecular process**.

In a bimolecular process the species collide with the necessary activation energy to give initially an **activated complex**. An activated complex is not a chemical substance which can be isolated, but consists of an association of the reacting particles in which bonds are in the process of being broken and formed. An activated complex breaks down to form either the products or reverts back to the original reactants.

The number of species taking part in any specified step in the reaction is known as the **molecularity**. In most cases the molecularity refers to the slowest step, that is the rate determining step.

In the reaction on the previous page, between nitrogen monoxide and hydrogen, the stoichiometry of the reaction involves two molecules of hydrogen and two molecules of nitrogen monoxide. Any proposed mechanism must be consistent with the rate expression. For third order reactions, such as this, the rate determining step will never be the first step. The proposed mechanism is:



If the first step was the slowest step the rate expression would be $\text{rate} = k[\text{NO}]^2$ and the rate would be zero order with respect to hydrogen. The rate for the second step depends on $[\text{H}_2]$ and $[\text{N}_2\text{O}_2]$. However, the concentration of N_2O_2 depends on the first step. So the rate expression for the second step becomes $\text{rate} = k[\text{H}_2][\text{NO}]^2$, which is consistent with the experimentally determined rate expression. The molecularity of the reaction is two, as two reacting species are involved in the rate determining step.

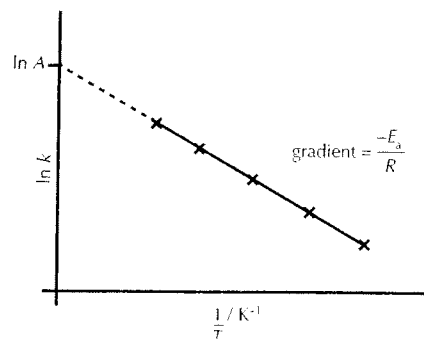
ARRHENIUS EQUATION

The rate constant for a reaction is only constant if the temperature remains constant. As the temperature increases the reactants possess more energy and the rate constant increases. The relationship between rate constant and absolute temperature is given by the Arrhenius equation:

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

where E_a is the activation energy and R is the gas constant. A is known as the Arrhenius constant and is related to the orientation of the reactants at the point of collision. This equation is often expressed in its logarithmic form:

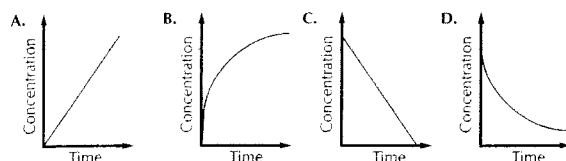
$$\ln k = \frac{-E_a}{RT} + \ln A$$



The equation can be used to determine both the Arrhenius constant and the activation energy for the reaction. This can be done either by substitution using simultaneous equations or by plotting $\ln k$ against $1/T$ to give a straight line graph. The gradient of the graph will be equal to $\frac{-E_a}{R}$ from which the activation energy can be calculated. Extrapolating the graph back to the $\ln k$ axis will give an intercept with a value equal to $\ln A$.

IB QUESTIONS – KINETICS

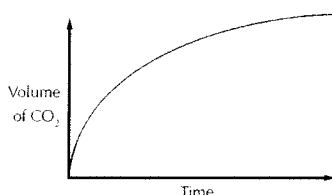
1. Which graph best represents the change in concentration of products with time for a reaction as it goes to completion?



2. Reactions between aqueous solutions of sodium thiosulfate and acid can be followed by timing the appearance of the solid sulfur that is produced. The time required for the appearance of sulfur would be increased by which of the following changes?

- A. Raising the temperature
B. Diluting the solution
C. Adding a catalyst
D. Increasing the concentration of the sodium thiosulfate

3. The reaction between excess calcium carbonate and hydrochloric acid can be followed by measuring the volume of carbon dioxide produced with time. The results of one such reaction are shown below. How does the rate of this reaction change with time and what is the main reason for this change?



- A. The rate increases with time because the calcium carbonate particles get smaller.
B. The rate increases with time because the acid becomes more dilute.
C. The rate decreases with time because the calcium carbonate particles get smaller.
D. The rate decreases with time because the acid becomes more dilute.
4. The rate of reaction of a strip of magnesium and 50 cm^3 of 1 mol dm^{-3} HCl is determined at 25°C . In which case would **both** new conditions contribute to an increase in the rate of reaction?
- A. Mg powder and 100 cm^3 of 1 mol dm^{-3} HCl
B. Mg powder and 50 cm^3 of 0.8 mol dm^{-3} HCl
C. 100 cm^3 of 1 mol dm^{-3} HCl at 30°C
D. 50 cm^3 of 1.2 mol dm^{-3} HCl at 30°C

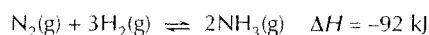
5. Calcium carbonate and hydrochloric acid react according to the equation below:



Which conditions will produce the fastest rate of reaction?

- A. 1 mol dm^{-3} HCl and CaCO_3 pieces
B. 2 mol dm^{-3} HCl and CaCO_3 pieces
C. 1 mol dm^{-3} HCl and CaCO_3 powder
D. 2 mol dm^{-3} HCl and CaCO_3 powder

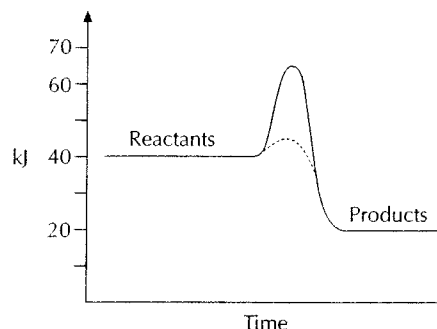
6. When ammonia is manufactured commercially a catalyst is used. What is the effect of this catalyst?



- I. To increase the rate of only the forward reaction
II. To increase the rates of the forward and reverse reactions
III. To shift the position of equilibrium and increase the yield of ammonia

- A. I only
B. II only
C. III only
D. I and III only

7. The energy diagram for a particular reaction under catalysed and uncatalysed conditions is shown below:



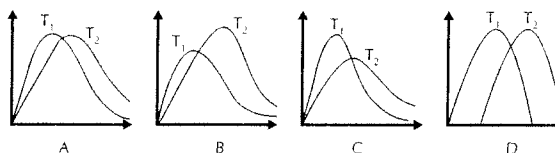
What are the value and sign of the enthalpy change for the catalysed forward reaction?

- A. -55 kJ B. -30 kJ C. -25 kJ D. -20 kJ

8. Some collisions between reactant molecules do not form products. This is most likely because

- A. the molecules do not collide in the proper ratio.
B. the molecules do not have enough energy.
C. the concentration is too low.
D. the reaction is at equilibrium.

9. Which graph shows the energy distribution for the particles of a gas when the temperature is **increased** from T_1 to T_2 ?



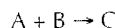
10. Which of the following is (are) important in determining whether a reaction occurs?

- I. Energy of molecules
II. Orientation of the molecules

- A. I only
B. II only
C. Both I and II
D. Neither I nor II

11. Doubling which one of the following will double the rate of a first order reaction?
- Concentrations of the reactant
 - Size of solid particles
 - Volume of solution in which the reaction is carried out
 - Activation energy

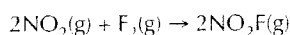
12. The kinetic data in the table below are for the reaction:



From these data what are the orders of the reaction with respect to A and B?

[A]	[B]	Initial Rate (mol dm ⁻³ sec ⁻¹)
0.1	0.1	1×10^{-5}
0.1	0.2	4×10^{-5}
0.2	0.1	1×10^{-5}

- order of A = 1 order of B = 0
 - order of A = 0 order of B = 2
 - order of A = 0 order of B = 4
 - order of A = 1 order of B = 2
13. The rate information below was obtained for the following reaction:

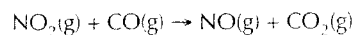


[NO ₂]/mol dm ⁻³	[F ₂]/mol dm ⁻³	Rate/mol dm ⁻³ s ⁻¹
0.001	0.005	2×10^{-4}
0.002	0.005	4×10^{-4}
0.002	0.010	8×10^{-4}

What are the orders for NO₂ and F₂?

- NO₂ is first order, F₂ is first order
- NO₂ is first order, F₂ is second order
- NO₂ is second order, F₂ is first order
- NO₂ is second order, F₂ is second order

14. Which factor(s) will influence the rate of the reaction shown below?



- The number of collisions per second
- The energy of the collisions
- The geometry with which the molecules collide

- I only
- II only
- I and II only
- I, II, and III

15. The rate constant for a certain reaction has the units **concentration time**⁻¹. What is the order of reaction?

- 0
- 1
- 2
- 3

16. Which reaction is an example of homogenous catalysis?

- $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \xrightleftharpoons{\text{Fe}(\text{s})} 2\text{NH}_3(\text{g})$
- $2\text{H}_2\text{O}(\text{aq}) \xrightarrow{\text{MnO}_2(\text{s})} 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightleftharpoons{\text{NO}(\text{g})} 2\text{SO}_3(\text{g})$
- $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Ni}(\text{s})} \text{C}_2\text{H}_6(\text{g})$

17. The rate-determining step of a reaction is the:

- fastest step in the reaction
- first step in the reaction
- final step in the reaction
- step with the highest activation energy.