

6 CHEMICAL KINETICS

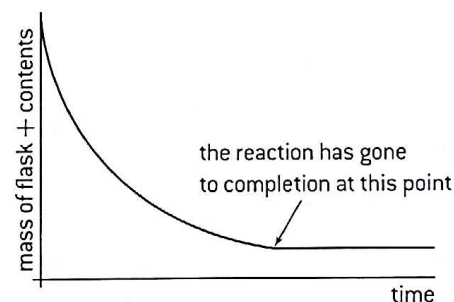
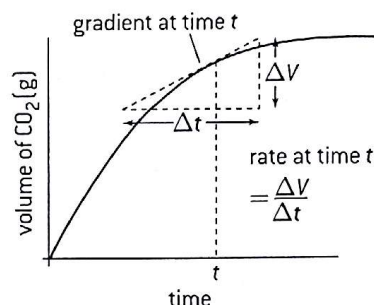
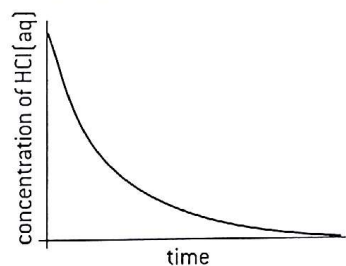
Rates of reaction and collision theory

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.

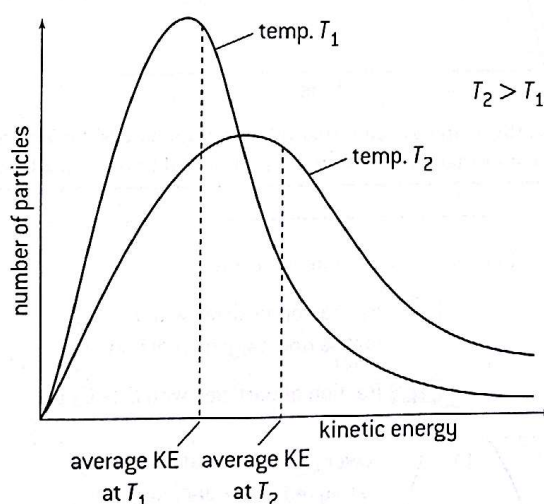
The reaction of hydrochloric acid with calcium carbonate can be used to illustrate three typical curves that could be obtained depending on whether the concentration of reactant, the volume of the product or the loss in mass due to the carbon dioxide escaping is followed.



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.

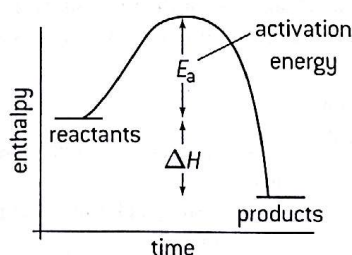
As the temperature increases, the area under the curve does not change as the total number of particles remains constant. More particles have a very high velocity resulting in an increase in the average kinetic energy, which leads to a broadening of the curve.



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.

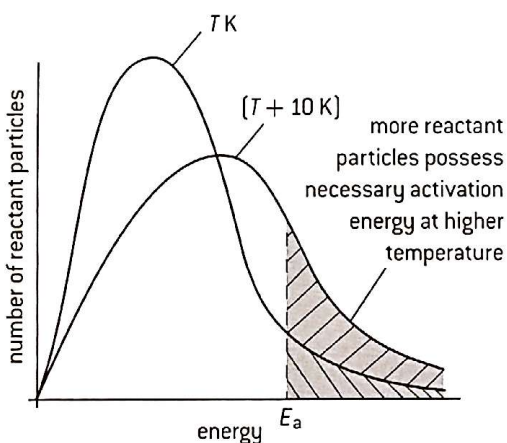
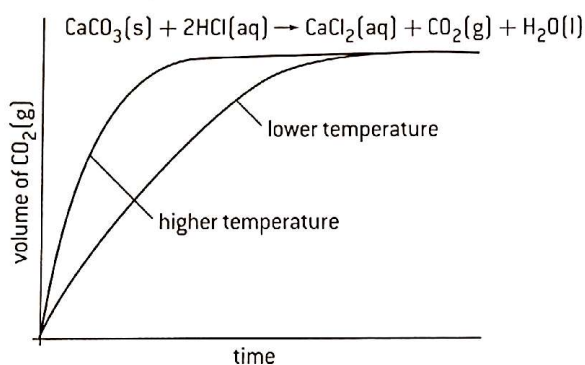


This minimum amount of energy required is known as the **activation energy**. Any factor that either increases the frequency of the collisions or increases the energy with which they collide will make the reaction go faster.

Factors affecting the rate of reaction

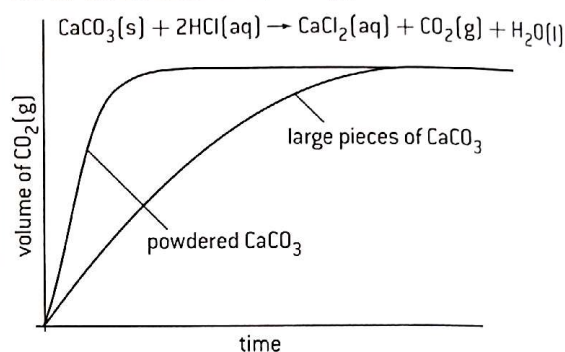
TEMPERATURE

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.



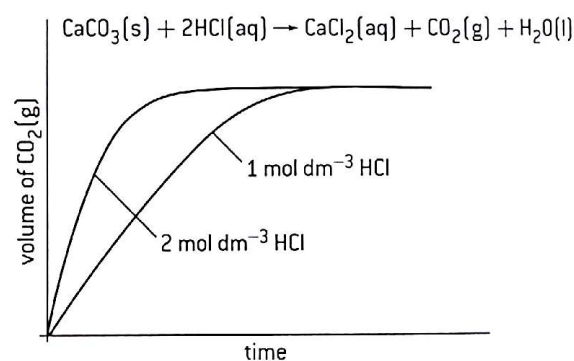
SURFACE AREA

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

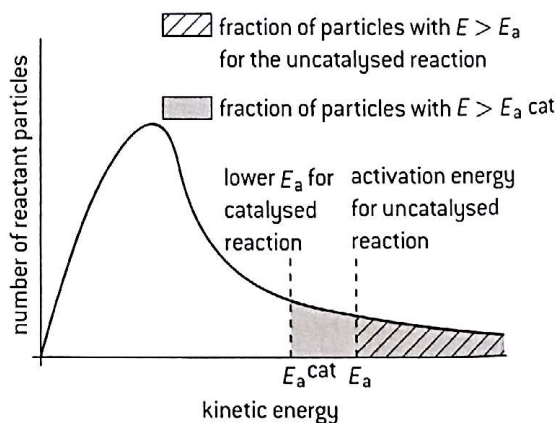
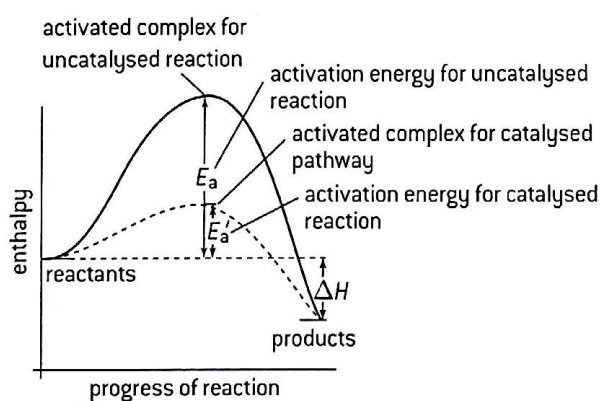
The more concentrated the reactants the more collisions there will be per second per unit volume. As the reactants get used up their concentration decreases. This explains why the rate of most reactions gets slower as the reaction proceeds. (Some exothermic reactions do initially speed up if the heat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





Rate expression and order of reaction

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

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

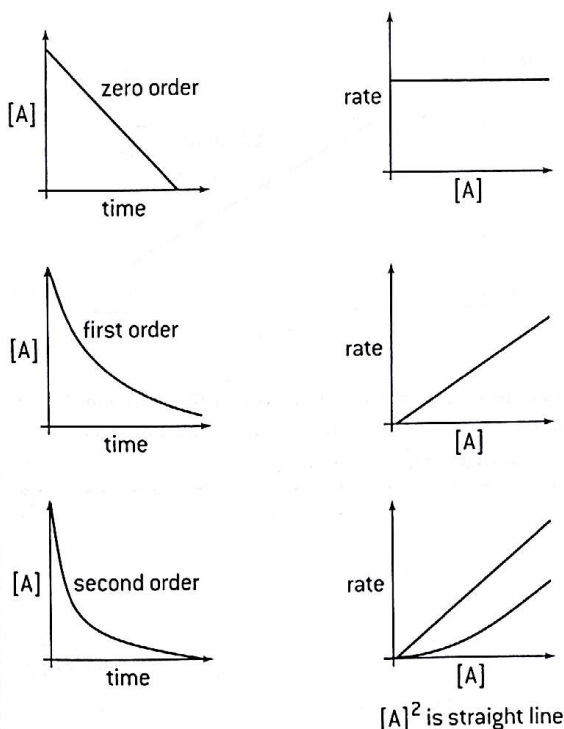
Second order: $\text{rate} = k[A]^2$ or $k = [A][B]$

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

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

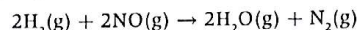
$$k = \frac{\text{rate}}{[A]^2[B]} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^3} = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

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 $\frac{d[A]}{dt} = k[A]$.

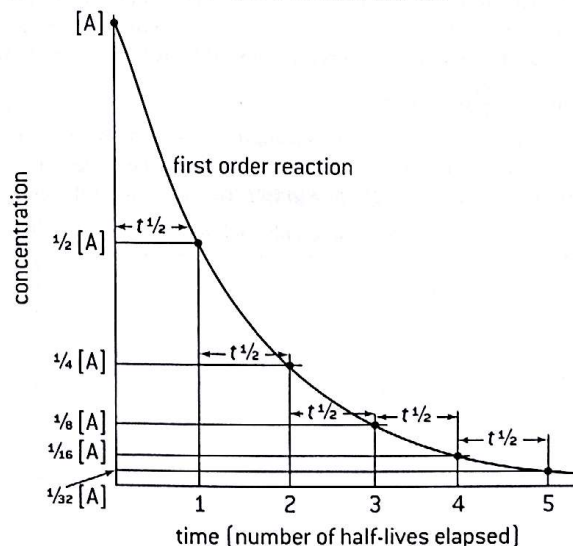
If this expression is integrated then $kt = \ln [A]_0 - \ln [A]$ where $[A]_0$ is the initial concentration and $[A]$ is the concentration at time t . This expression is known as the integrated form of the rate equation.

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 $kt_{1/2} = \ln [A]_0 - \ln \frac{1}{2}[A]_0 = \ln 2$ since $\ln 2 = 0.693$ this

$$\text{simplifies to } t_{1/2} = \frac{0.693}{k}$$

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:



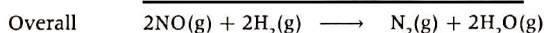
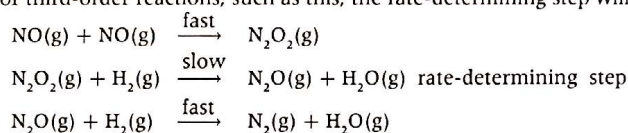
However fast $A-A$ reacts with B the rate of production of A_2B will only depend on how fast $A-A$ is formed.

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 either breaks down to form 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

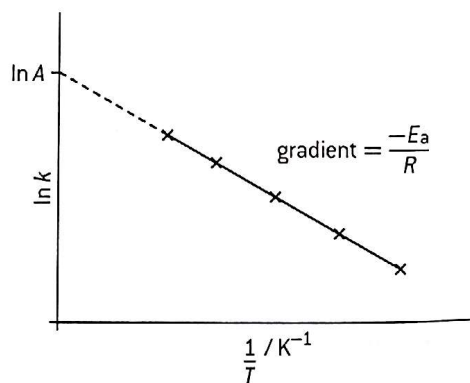
The rate constant for a reaction is only constant if the temperature remains constant. As the temperature increases the reactants possess more energy and the rate constant increases. The relationship between rate constant and absolute temperature is given by the Arrhenius equation:

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

where E_a is the activation energy and R is the gas constant. A is known as the frequency factor (or pre-exponential factor) and is indicative of the frequency of collisions with the correct orientation for the reaction to occur. This equation is often expressed in its logarithmic form:

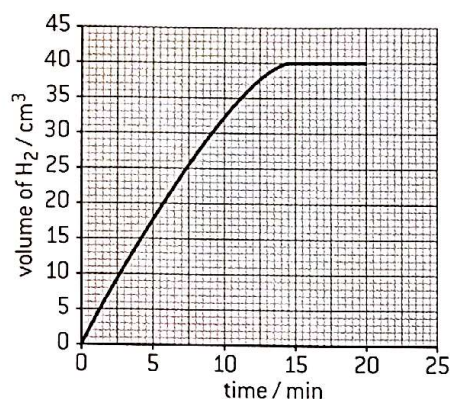
$$\ln k = \frac{-E_a}{RT} + \ln A$$

The equation can be used to determine both the frequency factor and the activation energy for the reaction. This can be done either by substitution using simultaneous equations or by plotting $\ln k$ against $\frac{1}{T}$ 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 $\ln A$.

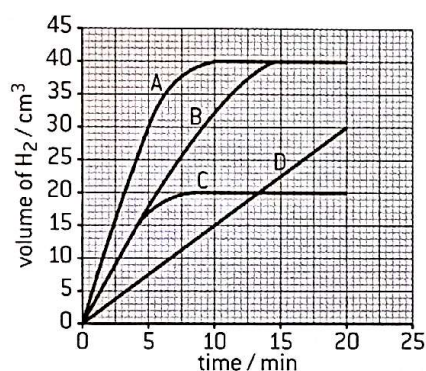


MULTIPLE CHOICE QUESTIONS – CHEMICAL KINETICS

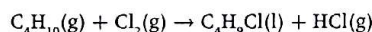
1. A piece of zinc was added to aqueous nitric acid and the volume of hydrogen gas produced was measured every minute. The results are plotted on the graph below.



Which graph would you expect if the same mass of powdered zinc was added to nitric acid with the same concentration?



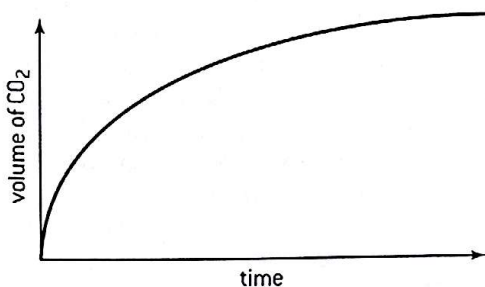
2. Which changes increase the rate of the reaction below?



- Increase of pressure
- Increase of temperature
- Removal of HCl(g)

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

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?

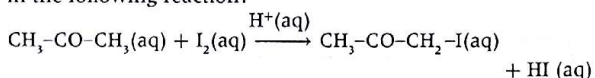


- The rate increases with time because the calcium carbonate particles get smaller.
- The rate increases with time because the acid becomes more dilute.

- The rate decreases with time because the calcium carbonate particles get smaller.
 - The rate decreases with time because the acid becomes more dilute.
4. Hydrochloric acid is reacted with large pieces of calcium carbonate, the reaction is then repeated using calcium carbonate powder. How does this change affect the activation energy and the collision frequency?

	Activation energy	Collision frequency
A.	increases	increases
B.	stays constant	increases
C.	increases	stays constant
D.	stays constant	stays constant

5. Which statement is true about using sulfuric acid as a catalyst in the following reaction?



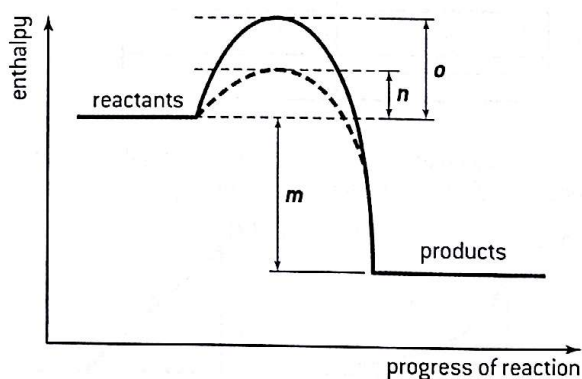
- The catalyst increases the rate of reaction.
- The catalyst lowers the activation energy for the reaction.
- The catalyst has been consumed at the end of the chemical reaction.

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

6. Which are appropriate units for the rate of a reaction?

- mol dm⁻³ s
- mol dm⁻³ s⁻¹
- mol dm⁻³
- s

7. The following enthalpy level diagram shows the effect of the addition of a catalyst to a chemical reaction. What do *m*, *n* and *o* represent?



	<i>m</i>	<i>n</i>	<i>o</i>
A.	ΔH	E_a (without a catalyst)	E_a (with a catalyst)
B.	E_a (with a catalyst)	ΔH	E_a (without a catalyst)
C.	E_a (with a catalyst)	E_a (without a catalyst)	ΔH
D.	ΔH	E_a (with a catalyst)	E_a (without a catalyst)

MULTIPLE CHOICE QUESTIONS – CHEMICAL KINETICS

8. Consider the reaction between magnesium and hydrochloric acid. Which factors will affect the reaction rate?

- I. The collision frequency of the reactant particles
- II. The number of reactant particles with $E \geq E_a$
- III. The number of reactant particles that collide with the appropriate geometry

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

9. What is the best definition of *rate of reaction*?

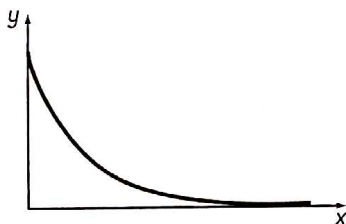
- A. The time it takes to use up all the reactants
 B. The rate at which all the reactants are used up
 C. The increase in concentration of a product per unit time
 D. The time it takes for one of the reactants to be used up



11. The decomposition of N_2O_5 occurs according to the following equation.

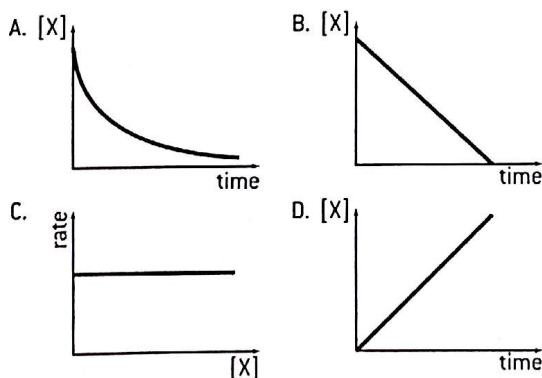


The reaction is first order with respect to N_2O_5 . What combination of variables could the axes represent on the graph below?



	x-axis	y-axis
A.	time	$[N_2O_5]$
B.	$[N_2O_5]$	time
C.	$[N_2O_5]$	rate of reaction
D.	rate of reaction	$[N_2O_5]$

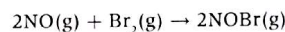
12. Which graph represents a reaction that is second order with respect to X for the reaction $X \rightarrow \text{products}$?



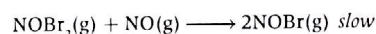
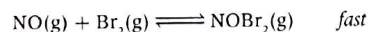
10. At 25°C , 200 cm^3 of 1.0 mol dm^{-3} nitric acid is added to 5.0 g of magnesium powder. If the experiment is repeated using the same mass of magnesium powder, which conditions will result in the same initial reaction rate?

	Volume of HNO_3 / cm^3	Concentration of $HNO_3 / \text{mol dm}^{-3}$	Temperature / $^\circ\text{C}$
A.	200	2.0	25
B.	200	1.0	50
C.	100	2.0	25
D.	100	1.0	25

13. Consider the reaction:



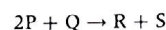
One suggested mechanism is:



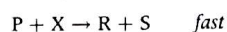
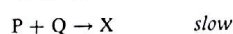
Which statements are correct?

- I. $NOBr_2(g)$ is an intermediate.
 - II. The second step is the rate-determining step.
 - III. $\text{rate} = k [NO]^2 [Br_2]$
- A. I and II only
 B. I and III only
 C. II and III only
 D. I, II and III

14. Consider the following reaction.



This reaction occurs according to the following mechanism.



What is the rate expression?

- A. $\text{rate} = k[P]$
 B. $\text{rate} = k[P][X]$
 C. $\text{rate} = k[P][Q]$
 D. $\text{rate} = k[P]^2[Q]$

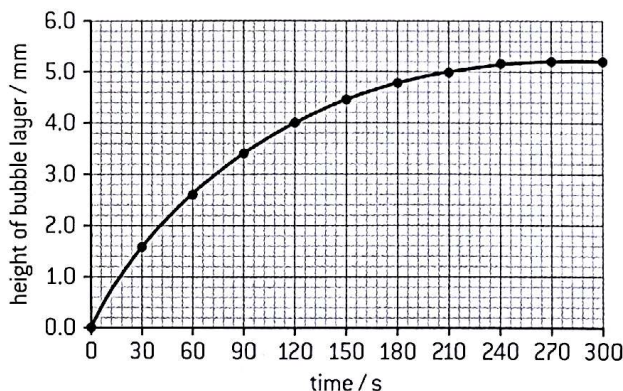
SHORT ANSWER QUESTIONS – CHEMICAL KINETICS

- Draw a graph that shows the distribution of molecular energies in a sample of a gas at two different temperatures, T_1 and T_2 such that T_2 is greater than T_1 . [2]
 - Define the term activation energy. [1]
 - State and explain the effect of a catalyst on the rate of an endothermic reaction. [2]
 - Magnesium is added to a solution of hydrochloric acid. Sketch a graph of acid concentration on the y-axis against time on the x-axis to illustrate the progress of the reaction. [1]
 - Describe how the slope of the line changes with time. [1]
 - Use the collision theory to state and explain the effect of decreasing concentration on the rate of the reaction. [2]
- Hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, releases oxygen gas, $\text{O}_2(\text{g})$, as it decomposes according to the equation:

$$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$

50.0 cm³ of hydrogen peroxide solution was placed in a boiling tube, and a drop of liquid detergent was added to create a layer of bubbles on the top of the hydrogen peroxide solution as oxygen gas was released. The tube was placed in a water bath at 75 °C and the height of the bubble layer was

measured every thirty seconds. A graph was plotted of the height of the bubble layer against time.



- Explain why the curve reaches a maximum. [1]
- Use the graph to calculate the rate of decomposition of hydrogen peroxide at 120 s. [3]
- The experiment was repeated using solid manganese(IV) oxide, $\text{MnO}_2(\text{s})$, as a catalyst.
 - Draw a curve on the graph above to show how the height of the bubble layer changes with time when manganese(IV) oxide is present. [1]
 - Explain the effect of the catalyst on the rate of decomposition of hydrogen peroxide. [2]



- Hydrogen and nitrogen(II) oxide react together exothermically as follows.

$$2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$$

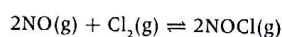
The rate of this reaction was investigated in a series of experiments carried out at the same temperature, the results of which are shown below.

Experiment	Initial $[\text{H}_2(\text{g})] / \text{mol dm}^{-3}$	Initial $[\text{NO}(\text{g})] / \text{mol dm}^{-3}$	Initial rate of reaction / $\text{mol dm}^{-3} \text{s}^{-1}$
1	2.0×10^{-3}	4.0×10^{-3}	4.0×10^{-3}
2	4.0×10^{-3}	4.0×10^{-3}	8.0×10^{-3}
3	6.0×10^{-3}	4.0×10^{-3}	
4	2.0×10^{-3}	2.0×10^{-3}	1.0×10^{-3}
5	2.0×10^{-3}	1.0×10^{-3}	

- Explain how the results from Experiments 1 and 2 can be used to deduce that the order of reaction with respect to hydrogen is 1. [1]
- Deduce the order of reaction with respect to nitrogen(II) oxide, giving a reason for your answer. [2]
- Use your answers from parts a) and b) to deduce the rate expression for the reaction. [1]
- Calculate the rate of reaction for each of Experiments 3 and 5. [2]
- Use the results from Experiment 1 to determine the value of, and the units for, the rate constant, k , for the reaction. [2]

- Suggest a mechanism for the reaction that is consistent with the rate expression. [2]
- The reaction is faster in the presence of a heterogeneous catalyst. Explain the meaning of the term heterogeneous as applied to a catalyst. Draw a labelled enthalpy level diagram that shows the effect of the catalyst. [3]

- The reaction between nitrogen(II) oxide and chlorine was studied at 263 K.



It was found that the forward reaction is first order with respect to Cl_2 and second order with respect to NO . The reverse reaction is second order with respect to NOCl .

- State the rate expression for the forward reaction. [1]
 - Predict the effect on the rate of the forward reaction and on the rate constant if the concentration of NO is halved. [2]
- Consider the following reaction.

$$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$$

Possible reaction mechanisms are:

Above 775 K: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ *slow*

Below 775 K: $2\text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ *slow*

$\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ *fast*

Based on the mechanisms, deduce the rate expressions above and below 775 K. [2]
 - State two situations when the rate of a chemical reaction is equal to the rate constant. [2]