

6.1 Collision theory and rates of reactions

- 6.1.1 Species react as a result of collisions of sufficient energy and proper orientation
- 6.1.2 The rate of reaction is expressed as the change in concentration of a particular reactant/product per unit time
- 6.1.3 Concentration changes in a reaction can be followed indirectly by monitoring changes in mass, volume and color
- 6.1.4 Activation energy (E_a) is the minimum energy that colliding molecules need in order to have successful collisions leading to a reaction
- 6.1.5 By decreasing E_a a catalyst increases the rate of a chemical reaction, without itself being permanently chemically changed
- 6.1.6 Descriptions of the kinetic theory in terms of the movement of particles whose average kinetic energy is proportional to temperature in Kelvin
- 6.1.7 Analysis of graphical and numerical data from rate experiments
- 6.1.8 Explanation of the effects of temperature, pressure/concentration and particle size on rate of reaction
- 6.1.9 Construction of Maxwell-Boltzmann energy distribution curves to account for the probability of successful collisions and factors affecting these, including the effect of a catalyst
- 6.1.10 Investigation of rates of reaction experimentally and evaluation of the results
- 6.1.11 Sketching and explanation of energy profiles with and without catalysts

Collision Theory

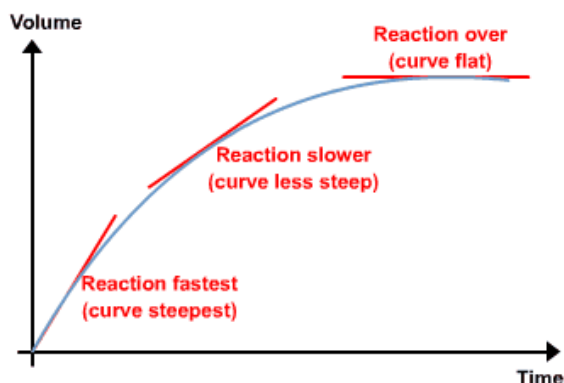
- For a reaction between two particles to occur three conditions must be met
 - The particles must collide
 - They must collide with the appropriate geometry or orientation
 - They must collide with sufficient energy to bring about the reaction
- The minimum amount of energy required is known as the activation energy

Factor	Effect of increasing factor	Explanation
Surface Area <i>Particle Size</i>	Decreases rate	The greater the particle size, the smaller the exposed surface area. Reactions require collisions for reactions to occur, so if the surface area is smaller, fewer collisions will occur per unit time
Temperature	Increases rate	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. Generally, an increase of 10°C doubles the rate of a chemical reaction
Concentration	Increases rate	Increasing the concentration increases the frequency of collisions which increases the frequency of successful collisions too, thus increasing the rate.
Pressure	Increases rate	Higher pressure compresses the gas, effectively increasing the concentration, so increasing the frequency of collisions and therefore the rate too.

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 as the **change in concentration of the products/reactants per unit time** or Increase/decrease in concentration of product/reacts per unit time

- Concentration changes in a reaction can be indirectly monitored by monitoring :
 - Change in volume of a gas, mass, concentration through titration, gas pressure or electrical conductivity
 - Calorimetry and light absorbance
- The results obtained is usually then plotted in a graph of concentration against time
- The rate at any point in time is the gradient of the graph at that time**
- Thus, find the gradient at t by using $\text{Rate of Reaction} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$



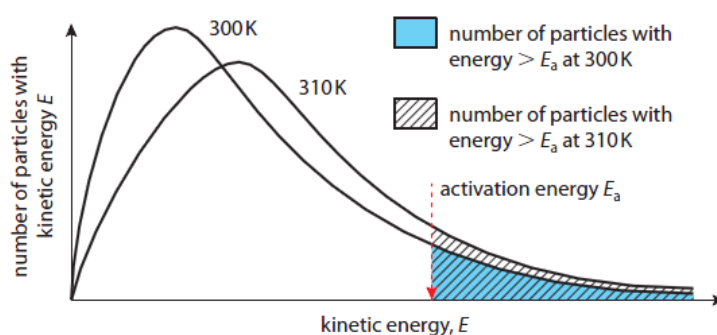
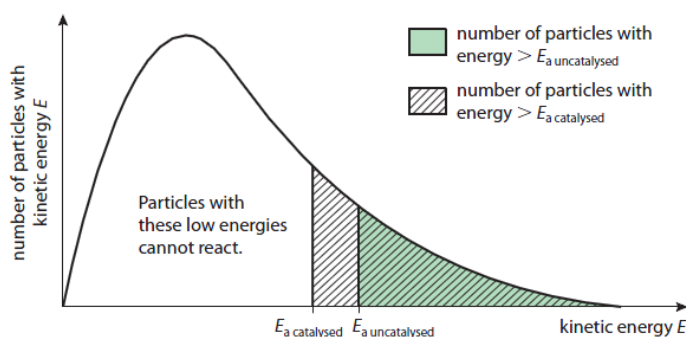
- The rate of reaction (gradient) will generally be the steepest at the start of the curve**
 - This is because a high concentration of reactant particles, therefore a high frequency of successful collisions
- The rate of reaction (gradient) decreases over time as time as the concentration of reactant particles decreases, thus the frequency of successful collisions also decreases**
- Hence, the rate of reaction can also be defined as:

The Rate of Disappearance of Reactants	The Rate of Formation of Products
$\text{Rate} = -\frac{\Delta[R]}{\Delta T}$ <p>Since Rate of Disappearance of Reactants is decreases over time, the negative sign counteracts this effect</p>	$\text{Rate} = \frac{\Delta[P]}{\Delta T}$ <p>This is the rate of which the products are formed</p>

- Where $\Delta[R]$ means the change in the concentration of R , and $\Delta[P]$ means the change in the concentration of P
- The units for rate of reactions are $\text{mol dm}^{-3} \text{s}^{-1}$

Maxwell-Boltzmann distribution curve

- The Maxwell-Boltzmann curve shows the distribution of kinetic energy for a reaction
- Only a small proportion of particles at a given temperature will have sufficient kinetic energy to overcome its E_a
- Activation energy (E_a): The minimum amount of energy required for a reaction to occur**
- As temperature increases, the area under the curve does not change as the total number of particles remains constant.
- Instead more particles have a very high velocity resulting in an increase in the average kinetic energy which leads to a broadening of the curve, however still has same activation energy
- Adding a catalyst reduces the activation energy, more particles have enough energy to react
 - If a species is both on the reactant and product side of the overall equation, it is probably a catalyst



16.1 Rate expression and reaction mechanism

Rate Expression

- The rate of reaction between two reactants, A and B, can be followed experimentally
- The mathematical relationship of reaction rate with reactant concentration can be expressed as a rate expression

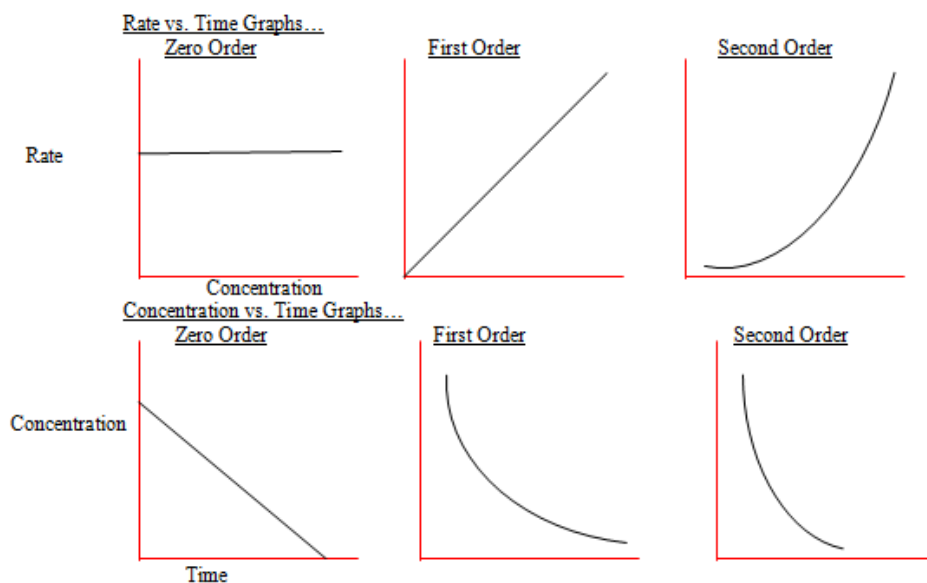
For the following hypothetical reaction: $aA + bB \rightarrow cC$

The Rate Law can be expressed as: $rate = k[A]^x[B]^y$

- The proportionality constant, k , is known as the rate constant
- The rate constant is different for each reaction and is **changed by temperature**
- The overall order of a reaction is: $order = x + y$
- For example, take: $rate = k[A][B]^2$. This reaction is third-order overall, first-order in A, and second order in B
- However, the order of a reaction and the rate expression can only be determined experimentally. They cannot be deduced from the balance equation
- Generally, reaction orders can be classified as zero-order, first-order, second-order and third-order:

Order:	Zero order	First order	Second order	Third order
Description	The rate does not depend on concentration	The rate is directly proportional to concentration If concentration doubles, rate doubles	The rate is proportional to the square of the concentration If the concentration doubles, rate quadruples	If the concentration doubles, the rate increases eight times
Rate Expression	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$ or Rate = $k[A][B]$	Rate = $k[A]^3$ or Rate = $k[A][B]^2$ or Rate = $k[A][B][C]$
Units of Rate	$= \text{mol dm}^{-3} \text{s}^{-1}$	$= \frac{\text{mol dm}^{-3} \text{s}^{-1}}{\text{mol dm}^{-3}}$ $= \text{s}^{-1}$	$= \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^2}$ $= \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$= \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^3}$ $= \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

- When graphed, reactions orders will be graphed as:



Activation energy

16.2

- 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. Where 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 reaction will depend only upon the rate of the slowest step
- The step with the highest activation energy will act as the rate determining step, which acts as a limit on the rate of reaction

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:

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

k: rate constant/A: Arrhenius constant/E_a: Activation energy/R: Gas constant/T: Temperature

- A graph of the Arrhenius equation allows us to calculate the activation energy of a reaction. We used the integrated version of the equation to simplify the graph into a linear expression ($y = mx + c$)

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

- The equation can be **used to determine both the frequency factor and the activation energy for a reaction**