

HL Reaction mechanisms and activation energy

REACTION MECHANISMS

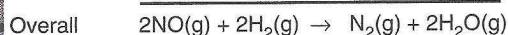
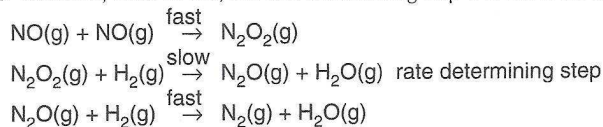
When the separate steps in a chemical reaction are analysed there are essentially only two types of processes. Either a single species can break down into two or more products by what is known as a **unimolecular process**, or two species can collide and interact by a **bimolecular process**.

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.

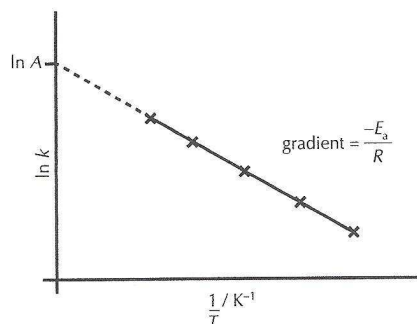
ARRHENIUS EQUATION

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 $\ln A$.

CATALYSIS

Catalysts provide an alternative pathway, so that the activation energy required to reach the activated complex is lowered.

Catalysts can be conveniently divided into two types.

- **Homogeneous catalysts** are in the same phase as the reactants and include examples such as concentrated sulfuric acid in the reaction between alcohols and carboxylic acids to form esters.
- **Heterogeneous catalysts** are in a different phase to the reactants. Common examples include metal catalysts in the presence of gases, e.g. nickel in the hydrogenation of alkenes and iron in the production of ammonia.

Heterogeneous catalysts tend to work by bringing the reactant particles into close alignment by adsorbing them onto the catalytic surface. In homogeneous catalysis the reactant particles are thought to form reversible complexes with the catalyst. Transition metals and their compounds are often good catalysts as the metals show variable oxidation states. Poisons work by forming irreversible complexes with the catalyst, which cause the active sites to become permanently blocked.

