

CHAPTER 23: Reaction Kinetics

23.1 Orders of Reaction and Rate Equations

23.2 Reaction Mechanisms

23.3 Catalysis

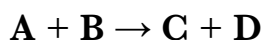
Learning outcomes:

- (a) *explain and use the terms: rate equation, order of reaction, rate constant, half-life of a reaction, rate-determining step.*
- (b) *construct and use rate equations of the form $\text{rate} = k[A]^m[B]^n$ (limited to simple cases of single step reactions and of multistep processes with a rate-determining step, for which m and n are 0, 1 or 2), including:*
 - (i) *deducing the order of a reaction from concentration-time graphs, by the initial rates method and half-life methods.*
 - (ii) *deducing, for zero- and first-order reactions, the order of reaction from concentration-time graphs.*
 - (iii) *verifying that a suggested reaction mechanism is consistent with the observed kinetics.*
 - (iv) *predicting the order that would result from a given reaction mechanism (and vice versa).*
- (c) *calculating an initial rate using concentration data. [integrated forms of rate equations are not required]*
- (d) (i) *show understanding that the half-life of a first-order reaction is independent of concentration.*
 - (ii) *use the half-life of a first-order reaction in calculations.*
- (e) *calculate a rate constant, for example by using the initial rates or half-life method.*
- (f) *devise a suitable experimental technique for studying the rate of a reaction, from given information.*
- (g) *outline the different modes of action of homogeneous and heterogeneous catalysis, including:*
 - (i) *the Haber process.*
 - (ii) *the catalytic removal of oxides of nitrogen in the exhaust gases from car engines.*
 - (iii) *the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide.*
 - (iv) *catalytic role of Fe^{3+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction.*

23.1 Orders of Reaction and Rate Equations

Rate Equation

- 1) The rate of reaction is dependent on the **concentration of the reactants**. Doubling the concentration may double or triple the rate of reaction, just to name a few.
- 2) A rate equation shows this relationship mathematically.
- 3) A rate equation **can only be obtained experimentally**, it cannot be deduced from the stoichiometric equation and it may not include all reactants written in the equation.
- 4) For a general reaction:



The rate equation is:

$$\boxed{\text{rate} = k[\mathbf{A}]^m[\mathbf{B}]^n}$$

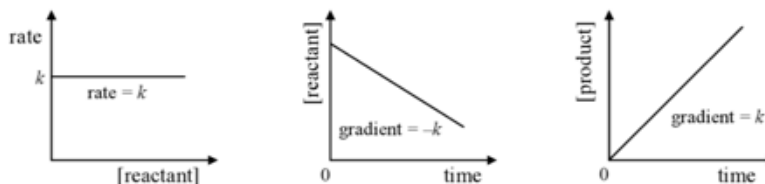
where k = rate constant
 m = order of reaction with respect to **A**
 n = order of reaction with respect to **B**
 $m + n$ = overall order of reaction

- 5) k is known as the **rate constant**, it is only a constant for a given reaction at a particular temperature. The unit of k depends on the rate equation and orders of reaction.
- 6) Note that the unit of rate is $\text{mol dm}^{-3} \text{s}^{-1}$ while the units of **[A]** and **[B]** are mol dm^{-3} .

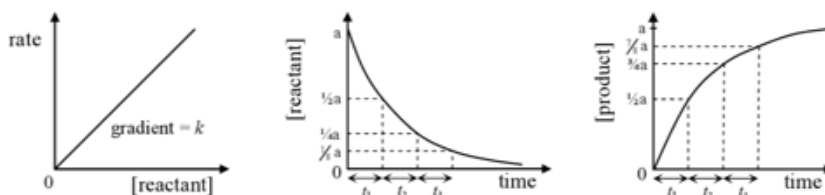
Order of reaction

- 1) The values m and n are known as the **orders of reaction**. Common values are 0, 1 and 2.
- 2) The *order of reaction* with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation.
- 3) Like rate equations, orders of reaction must be determined experimentally.

- 4) If a reaction is **zero-order** with respect to a reactant **A**:
- $m = 1$ and the rate equation becomes $\text{rate} = k[\mathbf{A}]^0[\mathbf{B}]^n = k[\mathbf{B}]^n$
 - The rate of reaction is independent of the concentration of A** because $[\mathbf{A}]^0 = 1$ and it disappears from the equation. Changing the concentration of **A** will not alter the rate of reaction.
 - The rate-concentration graph is a **horizontal line** showing the rate of reaction does not change.
 - The concentration-time graph is a **straight line with constant gradient** showing that rate is constant.



- 5) If a reaction is **first-order** with respect to a reactant **A**:
- $m = 1$ and the rate equation becomes $\text{rate} = k[\mathbf{A}][\mathbf{B}]^n$.
 - The rate of reaction is proportional to the concentration of A.** If $[\mathbf{A}]$ increases five times, the rate of reaction will increase five times as well.
 - The rate-concentration graph will show a **straight line through origin**.
 - The concentration-time graph will show a **curve with constant half-life**.



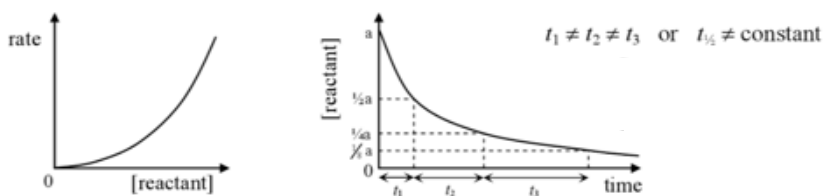
- Half-life, $t_{1/2}$* is the time taken for the initial concentration of reactant to decrease to half of its original value.
- Only a first-order concentration-time graph will show a curve with constant half-life. That is, $t_1 = t_2 = t_3 = t_{1/2}$.
- The relationship between half-life and rate constant is given by:

$$k = \frac{\ln 2}{t_{1/2}}$$

- 6) If a reaction is **second-order** with respect to a reactant **A**:
- $m = 2$ and the rate equation becomes $\text{rate} = k[\mathbf{A}]^2[\mathbf{B}]^n$.
 - The rate of reaction is proportional to the square of concentration of A.** If $[\mathbf{A}]$ increases five times, the rate of reaction will increase $5^2 = 25$

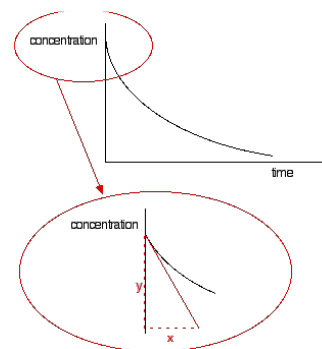
times.

- iii. - The rate-concentration graph is a **quadratic curve**.
- The concentration-time graph is a **curve with non-constant half-life**.



Deducing orders of reaction

- 1) Order of reaction must be determined experimentally, it can be deduced by either graphically or using initial rate experiments.
- 2) Deducing graphically involves plotting either a rate-concentration graph or concentration-time graph, and the order of a reaction may be deduced by looking at the pattern.
- 3) Using initial rate experiments, **the rate of reaction is measured at the very beginning of the experiment**. This is done by calculating the gradient of a concentration-time graph at the beginning.



- 4) A guide to find the order of reaction from the processed data:
Example 1:

Example 2 Using the data in the following table, find the order of reaction with respect to A, B and C, and the overall order of reaction. Write the rate equation and calculate a value for the rate constant including units.

Experiment	Concentrations (mol dm^{-3})			Rate of loss of A ($\text{mol dm}^{-3} \text{s}^{-1}$)
	A	B	C	
1	0.010	0.020	0.0050	1.4×10^{-6}
2	0.010	0.010	0.0050	7.0×10^{-7}
3	0.020	0.020	0.0050	1.4×10^{-6}
4	0.020	0.020	0.015	4.2×10^{-6}

Try to work this out yourself before you read any further.

Finding the orders of reaction

Compare experiments 1 and 3. The concentration of A has doubled but the other concentrations have not changed. There is no change in the rate.

The reaction is **zero order** with respect to A.

Now compare experiments 1 and 2 – all that has changed is the concentration of B. The concentration of B has halved between the two experiments, and so has the rate. (Check this on your calculator if you aren't sure.) Because what you do to the concentration of B has the same effect on the rate, the reaction is **first order** with respect to B.

Finally compare experiments 3 and 4. The only difference is that the concentration of C has tripled. So has the rate. The reaction is **first order** with respect to C.

The **overall order** is $0 + 1 + 1$, i.e. **second order overall**.

The rate equation

$$\text{Rate} = k[\text{B}][\text{C}]$$

Finding the rate constant k

Rearranging the rate equation gives:

$$k = \frac{\text{Rate}}{[\text{B}][\text{C}]}$$

Substituting values from the first experiment gives:

$$\begin{aligned} k &= \frac{1.4 \times 10^{-6}}{0.020 \times 0.0050} \\ &= 0.014 \end{aligned}$$

Finding the units for k

$$\begin{aligned} k &= \frac{\text{Rate}}{[\text{B}][\text{C}]} \\ &= \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} \\ &= \frac{\text{s}^{-1}}{\text{mol dm}^{-3}} \\ &= \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \end{aligned}$$

The value for k is therefore $0.014 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Example 2:

This is another example of a poorly designed series of experiments. This time it is made slightly more awkward because nothing turns out to be zero order.

Using the data in the table, find the order of reaction with respect to A and B.

Experiment	Concentrations (mol dm^{-3})		Rate of loss of A ($\text{mol dm}^{-3} \text{ s}^{-1}$)
	A	B	
1	0.10	0.10	1.0×10^{-3}
2	0.10	0.20	2.0×10^{-3}
3	0.30	0.30	9.0×10^{-3}

Finding the orders of reaction

Where to start? You cannot actually start with A this time because there isn't a pair of experiments in which the concentration of A changes while that of B remains the same – so you will have to start with B.

Between experiments 1 and 2, the concentration of B doubles and so does the rate. The reaction is **first order** with respect to B.

Now consider reactions 1 and 3. Both concentrations have changed, but you now know what effect the change in B would have. The concentration of B has tripled. That would triple the rate because the reaction is first order with respect to B.

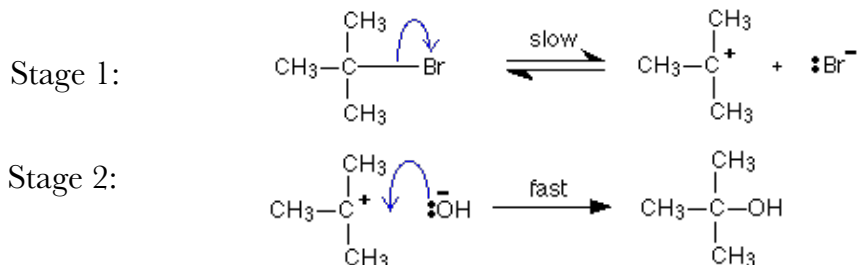
In fact the rate has increased 9 times – 3 times due to B, and therefore 3 times again due to A. This was caused by a tripling of the concentration of A, and so the reaction is **first order** with respect to A.

You could now go on to calculate k if you were asked to, but there is nothing new in this. If you want to practise doing it, the answer is $0.10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

23.2 Reaction Mechanisms

Rate-determining step

- 1) In any chemical change, some bonds are broken and new ones are made. Quite often, these changes are too complicated to happen in one simple stage. Instead, the reaction may involve a series of small changes one after the other.
- 2) A reaction mechanism describes the one or more steps involved in the reaction in a way which makes it clear exactly how the various bonds are broken and made.
- 3) The overall rate of reaction is governed by the **rate of the slowest step**. The slow step is therefore called the **rate-determining step**.
- 4) For example, the reaction between 2-bromo-2-methylpropane (a tertiary halogenoalkane) and hydroxide ion happens in two stages.



The overall equation is:



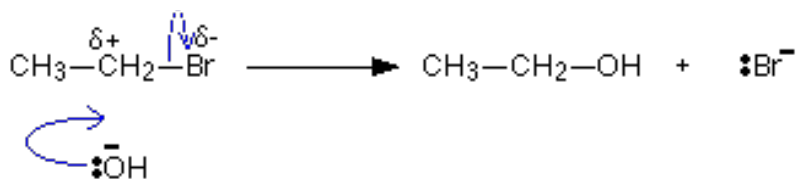
5) In this example, Step 1 is the rate-determining step because the rate of reaction depends entirely on the rate of this step. Increasing the rate of the already fast step 2 will not increase the overall rate of reaction.

6) By doing experiments, it can be found that the the rate equation is:

$$\text{rate} = [(\text{CH}_3)_3\text{CBr}]$$

The rate therefore does not depend on the hydroxide ion, which takes part in the second stage of the reaction.

7) Another example is the reaction between 1-bromoethane(a primary halogenoalkane) and hydroxide ion. This reaction happens in a single step.



8) The rate equation for this reaction is $\text{rate} = [\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$ because the rate of reaction depends on these two reactants.

Molecularity of reaction

- 1) *Molecularity of a reaction* is the number of species taking part in a (stage of) reaction.
- 2) i. In the first example above, Stage 1 has a molecularity of one because only one species is involved in this stage. Therefore Stage 1 is said to be **unimolecular**.
ii. Stage 2 involves two molecules colliding and therefore it has a molecularity of two. Stage 2 is said to be **bimolecular**.
- 3) In the second example, two species are involved, therefore it is a bimolecular reaction having a molecularity of two.

Order and mechanism

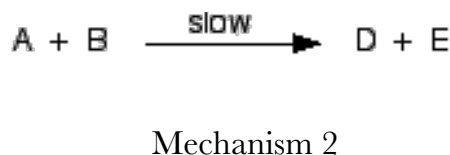
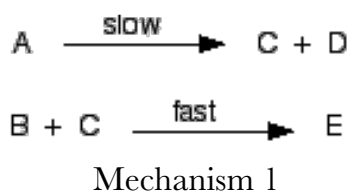
1) Given the rate equation and the orders of reaction, it is possible to deduce the reaction mechanism and vice versa.

2) i. For example, given:

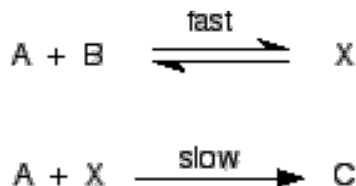
$$\text{rate} = k[\text{A}][\text{B}]$$

And given two possible reaction mechanisms. It can be deduced that mechanism 2 might be correct. This is because the rate equation tells us both A and B are involved in the rate-determining step (slow step) of the reaction.

ii. If we know that mechanism 2 is correct. We can deduce that the above rate equation might be the correct one, since two species are involved in the slow step.



3) i. If the rate-determining step is not the first step, for example:



ii. It can be deduced that the rate equation might be

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

iii. However, **X** is only an intermediate. Its concentration can be expressed in terms of concentrations of **A** and **B**, using the fact that the first step is in equilibrium.

iv. The steps are:

$$K_c = \frac{[\text{X}]}{[\text{A}][\text{B}]}$$

$$[\text{X}] = K_c [\text{A}][\text{B}]$$

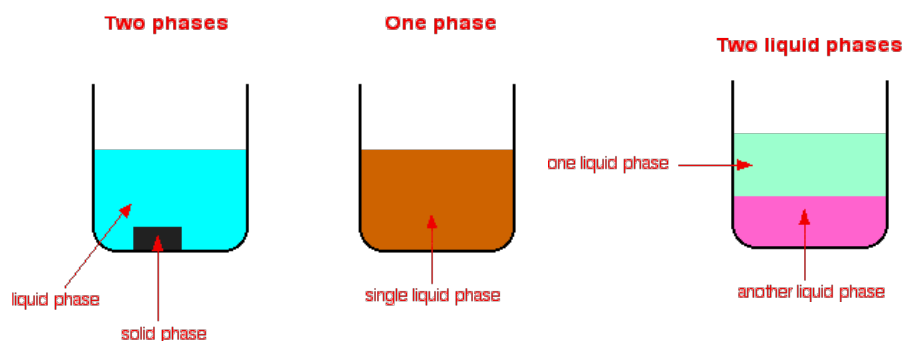
$$\text{Rate} = k[\text{A}] \times K_c [\text{A}][\text{B}]$$

$$\text{Rate} = k_1 [\text{A}]^2 [\text{B}]$$

23.3 Catalysis

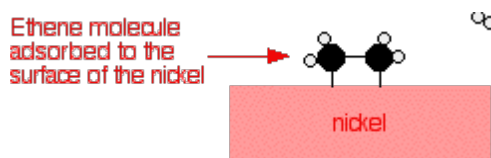
Phase and physical state

- 1) A *phase* is a region of space, throughout which all physical properties of a material are essentially uniform.
- 2) Examples of phases:

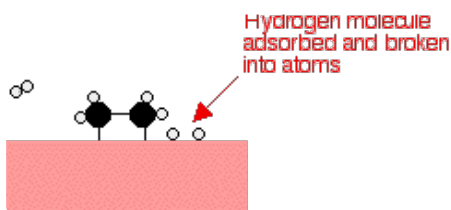


Heterogeneous catalysis

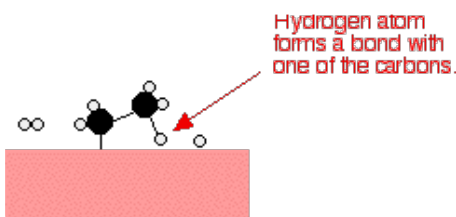
- 1) Heterogeneous catalysis involves **the use of a catalyst which is in different phase than the reactants**. Most often, the reactants are in gaseous state while the catalyst is in solid state.
- 2) In heterogeneous catalysis, the reactants are often **adsorbed** onto the surface of the active site of the catalyst.
- 3) Adsorption means 'sticking onto the surface'. A good catalyst should adsorb reactants strong enough but not so strong that the products cannot break away.
- 4) For example, the reaction between ethene and hydrogen is catalysed by nickel catalyst. Both ethene and hydrogen are gases while nickel is a solid.
 - i. Ethene molecules are **adsorbed** on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface.



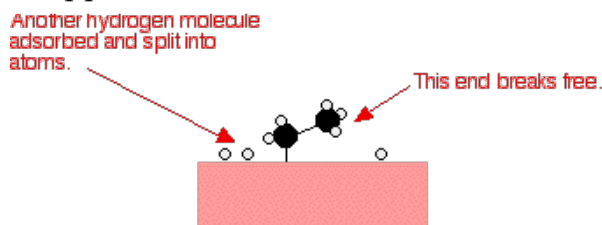
- ii. Hydrogen molecules are also adsorbed on to the surface of the nickel. When this happens, the hydrogen molecules are broken into atoms. These can move around on the surface of the nickel.



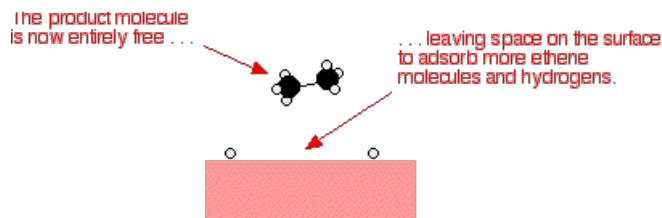
- iii. If a hydrogen atom diffuses close to one of the bonded carbons, the bond between the carbon and the nickel is replaced by one between the carbon and hydrogen.



- iv. That end of the original ethene now breaks free of the surface, and eventually the same thing will happen at the other end.



- v. As before, one of the hydrogen atoms forms a bond with the carbon, and that end also breaks free. There is now space on the surface of the nickel for new reactant molecules to go through the whole process again.

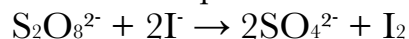


- 5) Most heterogeneous catalysts are transition elements or their compounds. This is because in transition elements, there are **empty/partially filled d-orbitals** available for the molecules to be adsorbed to.

Homogeneous catalysis

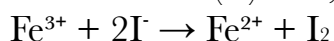
1) Homogeneous catalysis involves **the use of a catalyst which is in the same phase as the reactants.**

2) i. For example, the reaction between persulfate ions and iodide ions:



ii. This reaction proceeds very slowly because it involves two negative ions colliding.

iii. Iron(III) ions, Fe^{3+} is used as a catalyst. It oxidises the iodide ions into iodine molecules and itself is reduced to iron(II) ions, Fe^{2+} .



iv. The persulfate ions will oxidise the iron(II) ions into iron(III) ions and itself is reduced to sulfate ions.

