

26.1 RATE EQUATIONS, ORDER AND RATE CONSTANTS

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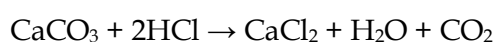
Learning outcomes

Candidates should be able to:

1. explain and use the terms rate equation, order of reaction, overall order of reaction, rate constant, half-life, rate-determining step, and intermediate
2. (a) understand and use rate equations of the form $\text{rate} = k [\text{A}]^m [\text{B}]^n$ (for which m and n are 0, 1 or 2)
(b) deduce the order of a reaction from concentration–time graphs or from experimental data relating to the initial rates method and half-life method
(c) interpret experimental data in graphical form, including concentration–time and rate–concentration graphs
(d) calculate an initial rate using concentration data
(e) construct a rate equation
3. (a) show understanding that the half-life of a first-order reaction is independent of concentration
(b) use the half-life of a first-order reaction in calculations
4. calculate the numerical value of a rate constant, for example, by:
(a) using the initial rates and the rate equation
(b) using the half-life, $t_{1/2}$, and the equation $k = 0.693/t_{1/2}$
5. For a multi-step reaction:
(a) suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction
(b) predict the order that would result from a given reaction mechanism and rate-determining step
(c) deduce a rate equation using a given reaction mechanism and rate-determining step for a given reaction
(d) identify an intermediate or catalyst from a given reaction mechanism
(e) Identify the rate-determining step from a rate equation and a given reaction mechanism
6. Describe qualitatively the effect of temperature change on the rate constant and hence the rate of a reaction

Initial assessment

1. Explain the meaning of the terms: *rate of reaction*, *frequency*, *effective collisions*, and *non-effective collisions*.
2. Write a paragraph using ideas about colliding particles to explain the effect of increasing the concentration of a reactant on the rate of reaction and decreasing the temperature on the rate of reaction.
3. Work with a group of other learners to suggest three different methods of monitoring the rate of a reaction.
4. Write a paragraph about how catalysts increase the rate of a chemical reaction.
5. Sketch a reaction pathway diagram for an endothermic reaction in the presence and absence of a catalyst.
6. Explain how you can find the rate of reaction at any one time from a graph of volume of gas (y -axis) against time (x -axis).
7. Draw and explain the shape of the graph obtained by plotting the loss in mass of the reaction mixture with time for the reaction



Introduction

Rate of reaction

We calculate the *rate of reaction* by measuring a decrease in the concentration of a particular reactant or an increase in the concentration of a particular product over a period of time.

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{time taken}}$$

Units of concentration are usually expressed in mol dm^{-3} , and units of time are usually expressed in seconds. Therefore, the units of the reaction rate are typically $\text{mol dm}^{-3} \text{ s}^{-1}$.

Imagine an experiment:

Experiment [A] / mol dm^{-3} [B] / mol dm^{-3} Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$

1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	4.0×10^{-3}
3	0.10	0.20	8.0×10^{-3}

What is controlling the rate of this reaction?

The **rate equation** is an expression showing how the rate of reaction is linked to the concentration of the reactants. The rate is equal to the rate constant (k) multiplied by the concentration of each reactant raised to certain whole-number powers (called orders).

The rate equation for the general reaction $\text{P} + \text{Q} \rightarrow \text{R} + \text{S}$ is:

$$\text{rate} = k[\text{P}]^x [\text{Q}]^y$$

where x is the **order of reaction** with respect to reactant P, y is the order of reaction with respect to reactant Q, and k is the **rate constant**.

Rate equation: an equation showing the relationship between the rate constant and the concentrations of the species that affect the rate of reaction.

Rate constant: the proportionality constant, k , in a rate equation

The **overall order of the reaction** is the sum of all the orders in the rate equation. For this reaction, the overall order of reaction would be $x + y$.

Rate has units of $\text{mol dm}^{-3} \text{ s}^{-1}$.

Concentration has units of mol dm^{-3} .

The units of the rate constant, k , depend on the overall order of the reaction, and the units can be calculated.

Order of reaction: the power to which the concentration of the reactant is raised in the rate equation. If a rate is directly proportional to concentration, it is a first-order reaction; if the rate is directly proportional to the square of the concentration, it is a second-order reaction. The overall order of reaction is the sum of these powers.

REMEMBER that the units of rate are usually mol dm^{-3} , but the units of rate constant must be worked out from the rate equation.

Pseudo first order reaction

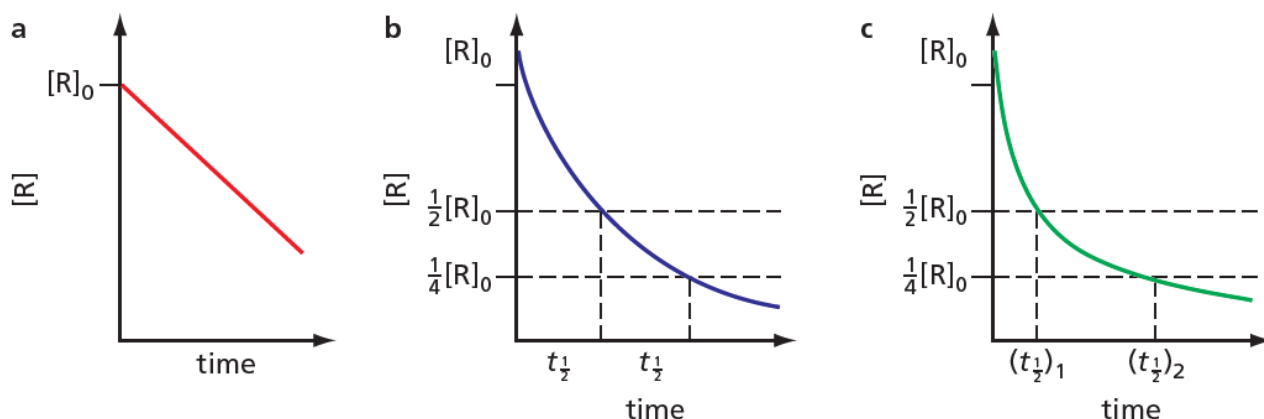


Figure: The three most common types of concentration-time graphs: **a** zero order, **b** first order, **c** second order. $[R]_0$ is the concentration at time $t = 0$.

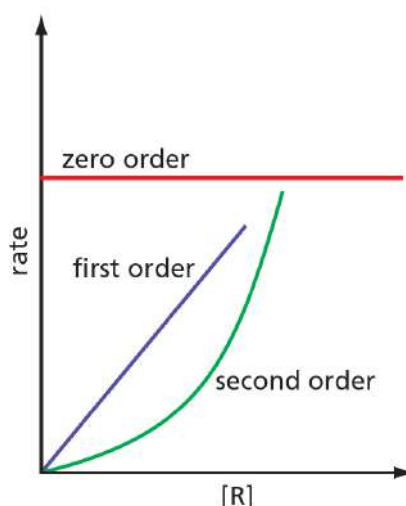


Figure: Rate-concentration graphs can be used to distinguish between zero-order, first-order, and second-order reactions.

The zero-order graph is a straight line parallel to the x-axis.

The first-order graph is a straight line passing through the origin.

The second-order graph is a parabola starting at the origin.

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Effect of temperature change on the rate constant

Half life

Half-life $t_{1/2}$: time taken for the amount (or concentration) of the limiting reactant in a reaction to decrease to half its initial value.

First-order reactions have a fixed half-life time, which is given by the following relation:

$$k = 0.693/t_{1/2}$$

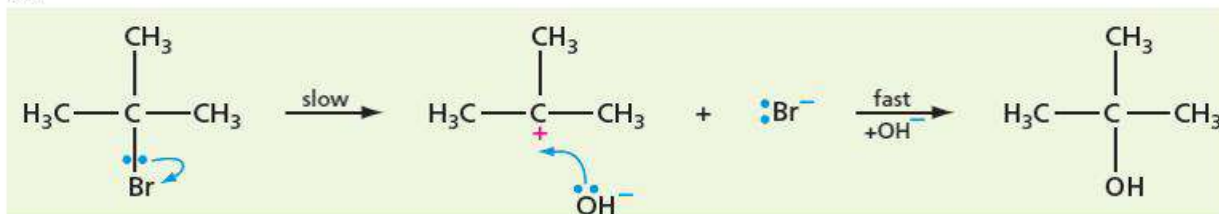
The half-life of a second-order reaction is not constant; it changes with time.

For a multi-step reaction

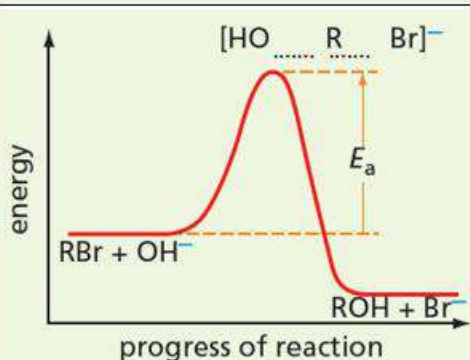
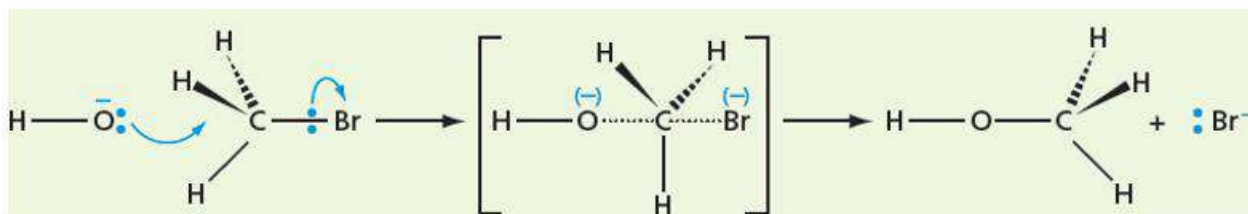
Rate-determining step: the slowest step in a reaction mechanism

Chem Demo: Reaction Mechanism and Rate - YouTube

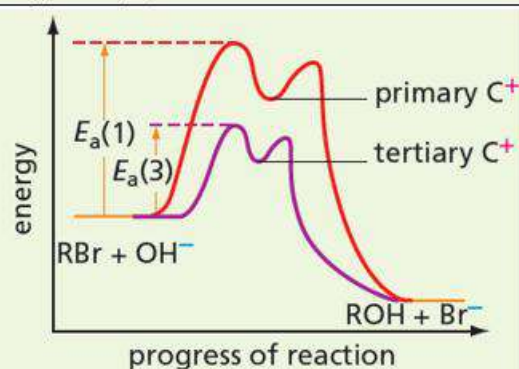
SN¹



SN²



▲ Figure 16.10 Reaction profile for the S_N2 hydrolysis of bromomethane



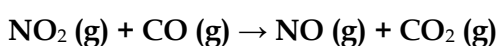
▲ Figure 16.11 Reaction profiles for the S_N1 hydrolysis of primary and tertiary bromoalkanes

Predicting the reaction mechanism

The **overall reaction equation** and **rate equation** can be used to predict a possible reaction mechanism of a reaction

For example, nitrogen dioxide (NO₂) and carbon monoxide (CO) react to form nitrogen monoxide (NO) and carbon dioxide (CO₂)

The overall reaction equation is:



The rate equation is:

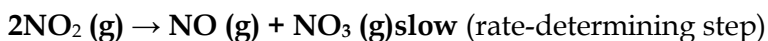
$$\text{Rate} = k [\text{NO}_2]^2$$

From the rate equation, it can be concluded that the reaction is **zero order** with respect to CO (g) and **second order** with respect to NO₂ (g)

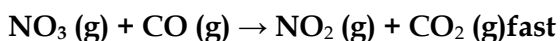
This means that there are **two molecules** of NO₂ (g) involved in the **rate-determining step**

A possible reaction mechanism could therefore be:

Step 1:



Step 2:



Overall:



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

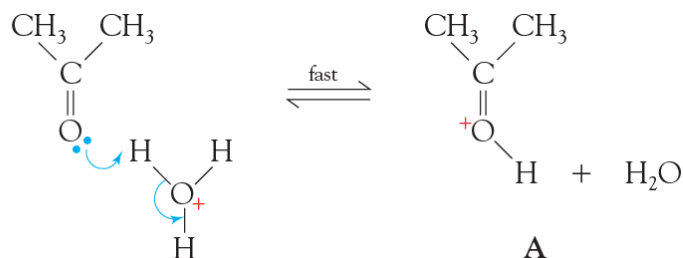
Proposing a mechanism

The rate equation is often used as a basis for suggesting a likely mechanism for the reaction. Most reactions can be broken down into a number of steps, one of which has a high activation energy that determines the overall rate of the reaction. This step is called the **rate-determining step**. An analogy is a group of people buying a paper at the local newsagent. If one person arrives, it takes them 1 second to pick up the paper, 10 seconds to pay for it and 1 second to leave the shop. If ten people arrive at the same time, it takes 10 seconds for them all to pick up their paper and 100 seconds for them all to pay, but they still take only 1 second each to leave the shop. There will be a queue to pick up the paper and at the checkout, but not on the way out of the shop. Any step that takes place after the rate-determining step has no effect on the overall rate. In the rate equation for the iodination of propanone,

$$\text{rate} = k[\text{I}_2]^0[\text{H}^+]^1[\text{CH}_3\text{COCH}_3]^1$$

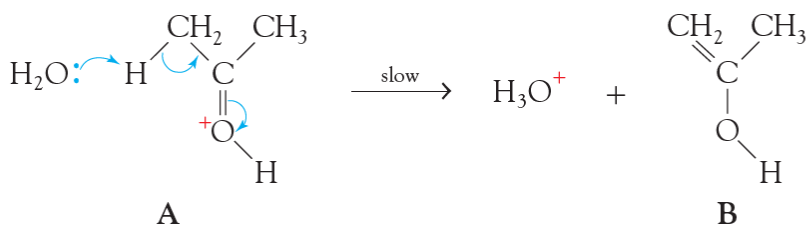
iodine does not appear in the rate equation, so any step involving iodine must come after the rate-determining step. It is also reasonable to conclude that the first step is the reaction of a proton with propanone, as both H^+ and CH_3COCH_3 appear as first-order terms in the rate equation. This reaction is an acid-base reaction. Such reactions are usually fast and reversible (H^+ exists as H_3O^+ in aqueous solution). So we write:

Reaction 1



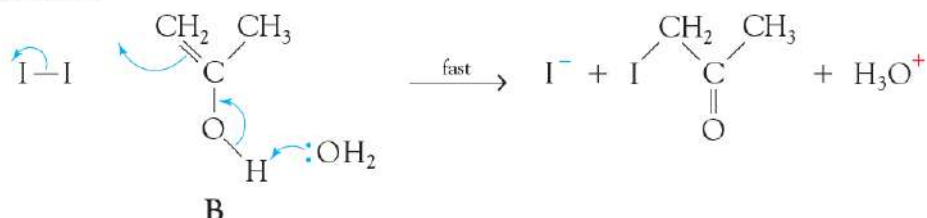
The second step, involving the breaking of a C—H bond, probably controls the rate of the reaction: C—H bond breaking is known to be much slower than O—H bond breaking. In this step, a water molecule could act as a base, taking a proton off the protonated propanone and re-forming H_3O^+ . A possible second step is therefore:

Reaction 2



Iodine reacts rapidly with compounds containing the $\text{C}=\text{C}$ group, so a fast step follows:

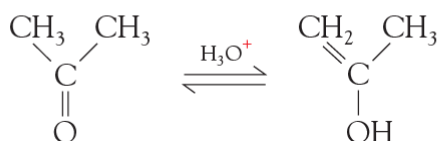
Reaction 3



Adding up all the individual steps in the mechanism, we arrive at the overall stoichiometric equation:

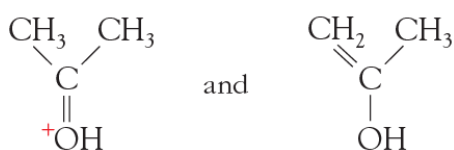


Mechanistically we can define a **homogeneous catalyst** as a substance that appears in the rate equation but not in the stoichiometric equation. If we consider just the first two steps, of which the second is the rate-determining step, H_3O^+ is a homogeneous catalyst.



Note, however, that the last of the three steps described above produces $\text{H}^+(\text{aq})$, which, as we have seen, is the catalyst for the first two steps. A reaction which produces its own catalyst like this is called an **autocatalytic reaction**.

Substances such as:



are known as **intermediates**, because they are produced during the reaction but are not part of the final products.

[orders of reaction and mechanisms](#)

[Is it a Catalyst or an Intermediate? \(Given Mechanism\) - YouTube](#)

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