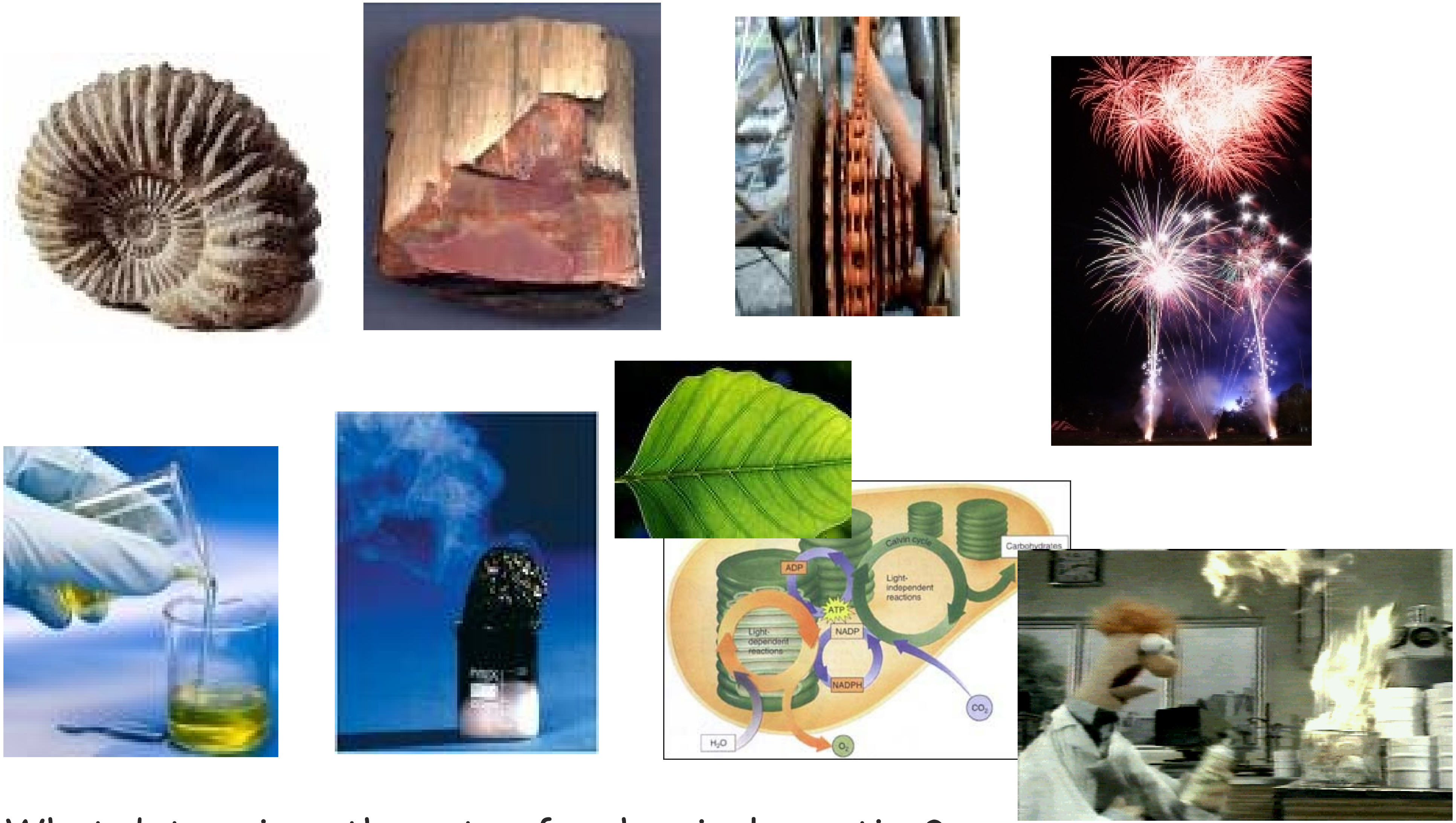
Chemical reaction rates



What determines the rate of a chemical reaction?
How do we measure the rate of a chemical reaction?
How can we use the data to understand the reaction mechanism?

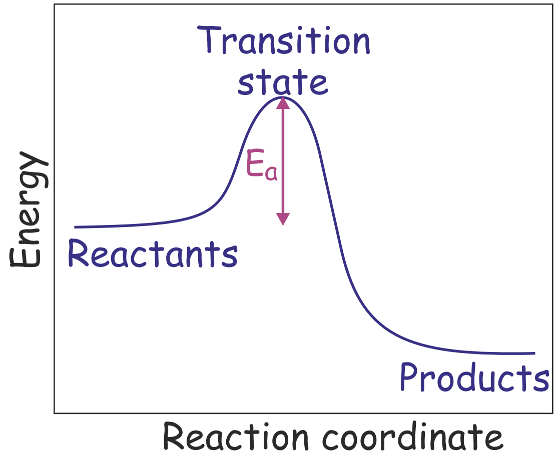
Elementary reactions

These are the most fundamental chemical processes. There are various types:

Unimolecular - dissociation or isomerisation

Bimolecular - reactive collisions between two atoms, molecules or ions

Termolecular - reactive collisions between three atoms, molecules or ions (rare and often requires high pressures)



- All involve a transition between two atomic or molecular states separated by a potential energy barrier.
- Barrier height determines rate and temperature dependence.

- Overall reaction equations usually represent the net result of a number of elementary steps.

  <u>There is often no single-step process corresponding to the reaction equation</u>

Chemical kinetics studies

A study into the kinetics of a chemical reaction is usually carried out with one or both of the following goals in mind:

- Analysis of the sequence of elementary steps making up the overall reaction i.e. determination of the kinetic mechanism.

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ \underline{ClO + O \rightarrow Cl + O_2} \\ O_3 + O \rightarrow 2O_2 \end{array}$$

- Determination of the absolute rate of the reaction and/or its individual elementary steps

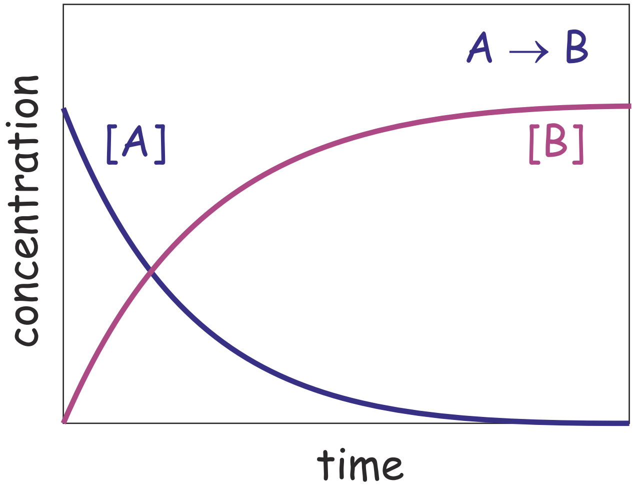
The aim of this course is to show you how both of these goals may be achieved.

Rate of reaction

- Rate at which reactants are used up or products are formed.

- Units of either concentration per unit time (mol dm^{-3} s^{-1}) or pressure per unit time (Pa s^{-1}, mbar s^{-1} or Torr s^{-1})

Note: from the ideal gas law, $c = \frac{n}{V} = \frac{p}{RT}$, so dividing the rate in pressure units by RT yields the rate in concentration units.



The rate is simply the slope of a plot of reactant or product concentration vs time

$$\text{rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Note that the rate is time dependent

Rate of reaction - correction for reaction stoichiometry

Consider the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

According to our current definition, we could define the rate of reaction in terms of the rate of change of concentration of N_2, H_2 or NH_3.

If the rate of change of $[N_2]$ is x, then we have

$$-\frac{d[N_2]}{dt} = x \text{ mol dm}^{-3}\text{ s}^{-1}.$$

$$-\frac{d[H_2]}{dt} = 3x \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{d[NH_3]}{dt} = 2x \text{ mol dm}^{-3}\text{ s}^{-1}$$

Three different rates for the same reaction!

To solve this problem, we define the reaction rate as the rate of change of a reactant or product concentration divided by its stoichiometric coefficient.

$$\nu = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Simple rate laws

- A rate law is an expression that relates the reaction rate to the concentrations of the chemical species present in the reaction mixture, may include reactants, products and catalysts (but not reactive intermediates).

- Many reactions follow a simple rate law...

rate constant

$$\nu = k\,[A]^a[B]^b[C]^c\ldots$$

orders w.r.t each species (may be non-integer)

... in which the rate is proportional to the product of the concentrations raised to some power. The overall order is the sum of the individual orders.

- Elementary processes always follow simple rate laws, which we can write down directly from the reaction equation.

unimolecular	$A \rightarrow B$	$\nu = k\,[A]$
bimolecular	$A + B \rightarrow P$	$\nu = k\,[A][B]$
	$A + A \rightarrow P$	$\nu = k\,[A][A] = k\,[A]^2$

- For elementary reactions, the orders reflect the molecularity of the process.

Complex rate laws

- Many complex (i.e. multi-step) reactions also follow simple rate laws. e.g.

$H_2 + I_2 \rightarrow 2HI \qquad \nu = k\,[H_2][I_2]$

$3ClO^- \rightarrow ClO_3^- + 2Cl^- \qquad \nu = k\,[ClO^-]^2$

Note: these <u>do not</u> follow directly from the reaction equation.

- Other reactions follow complex rate laws. These often contain more than one rate constant and show a much more complicated dependence on concentration. e.g.

$$H_2 + Br_2 \rightarrow 2HBr \qquad \nu = \frac{[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

-First order w.r.t. $[H_2]$
-No overall order

- A complex rate law <u>always</u> indicates a multi-step reaction mechanism.

$Br_2 \rightarrow Br + Br$
$Br + H_2 \rightarrow H + HBr$
$H + Br_2 \rightarrow Br + HBr$
$Br + Br \rightarrow Br_2$

slightly simplified version of the kinetic mechanism for the above reaction.

Note: the units of the rate constant

- Rate constants for different reactions often have different units, depending on the concentrations appearing in the rate law.

Examples:

1. A second order rate law $\nu = k[H_2][I_2]$

   Since we know that the rate has units of mol dm^{-3} s^{-1} (concentration per unit time) and the concentrations are in mol dm^{-3}, we can easily work out the units of k.

   units of k

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

$$\text{so} \quad [k] = \frac{(\text{mol dm}^{-3}\ \text{s}^{-1})}{(\text{mol dm}^{-3})\ (\text{mol dm}^{-3})} = \text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$$

2. A first order rate law $\nu = k[CH_3N_2CH_3]$

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

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

Note: the units of the rate constant

3. An order 3/2 rate law $\nu = k[CH_3CHO]^{3/2}$

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

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

An important point:

It is meaningless to try comparing two rate constants unless they have the same units!

(you wouldn't try to compare 10 m with 4 kg)

Integrated rate laws

- A rate law is a differential equation that describes the rate of change of a reactant (or product) concentration with time.

- If we integrate the rate law we obtain an expression for the concentration as a function of time, which may be compared directly with experimental data.

- Often, the rate law must be integrated numerically, but there are a number of simple cases in which the integration may be carried out analytically.

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2}\frac{d[A]}{dt} = -k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k\,[A][B]$	$-kt = \frac{1}{[B]_0-[A]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$

Half lives

- The half life of a substance, $t_{1/2}$, is the time it takes for the concentration of the substance to fall to half of its initial value.

Note that it only makes sense to define a half life for a substance not present in excess at the start of the reaction.

- We can find an expression for the half life of a substance by substituting the values ($t = t_{1/2}$, $[A] = [A]_0/2$) into the appropriate integrated rate law.

zeroth order $t_{1/2} = \dfrac{[A]_0}{2k}$

After one half life has elapsed, the new starting concentration is $[A]_0/2$, so successive half lives decrease by a factor of two

first order $t_{1/2} = \dfrac{\ln 2}{k}$

The half life has no concentration dependence, so successive half lives are identical.

second order $t_{1/2} = \dfrac{1}{k[A]_0}$

Inverse dependence on concentration, so successive half lives double.

The relationship between rate law and mechanism

- For a single step (elementary) reaction, the rate law follows directly from the reaction equation.

- For a multi-step reaction, the rate law does <u>not</u> follow directly from the reaction equation, since this equation is simply the net result of all of the elementary steps.

- The rate law for a multi-step reaction does, however, follow directly from the sequence of elementary steps, and is therefore our best tool for determining an unknown mechanism.

    - If we know the sequence of elementary steps, we can deduce the rate law.

    - If we don't know the sequence of elementary steps, we can compare the rate laws predicted from one or more trial mechanisms with experimental data (e.g. rate constants and reaction orders).

Kinetic studies

How do we measure the rate of a chemical reaction?

1. Mix the reactants and initiate reaction on a timescale that is negligible relative to that of the reaction.

2. Monitor the concentration(s) of one or more reactants and/or products as a function of time.

3. Since rate constants change with temperature, the temperature must be accurately measured and controlled.

- Many techniques have been developed to cover the huge range of timescales over which chemical reactions occur.

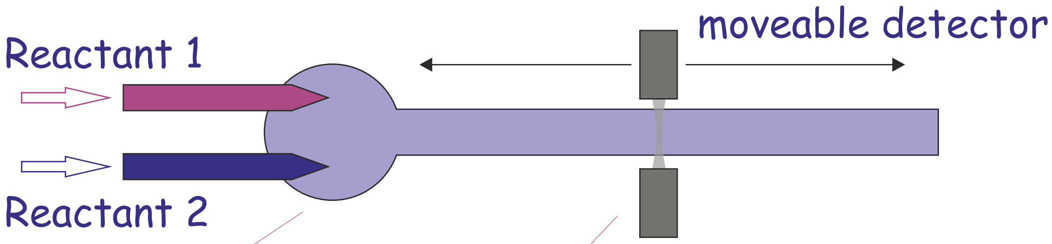
Batch techniques - reaction initiated at a well-defined time and concentrations are followed as a function of time after initiation.

Continuous techniques - reaction continuously initiated and time dependence of reaction mixture composition inferred from concentrations in different regions of the reaction vessel or other means.

Techniques for mixing reactants and initiating reaction

Continuous flow techniques

- May be used to study reactions occurring on time scales of s to ms.

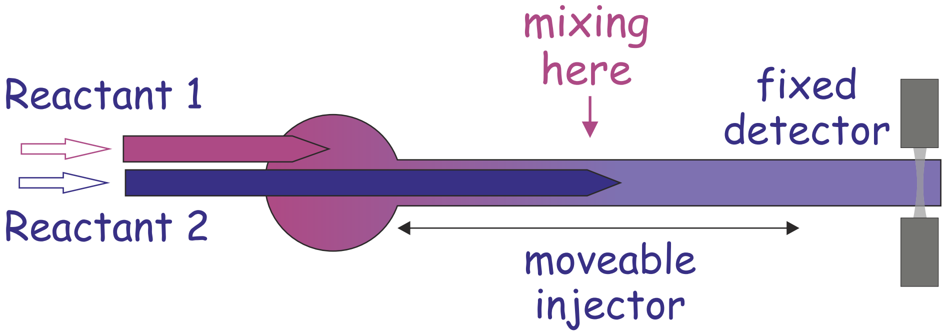


Mix reactants at start of flow tube

Measure composition at different positions along flow tube ⇒ Convert position to time using known flow velocity

$t = d/v$

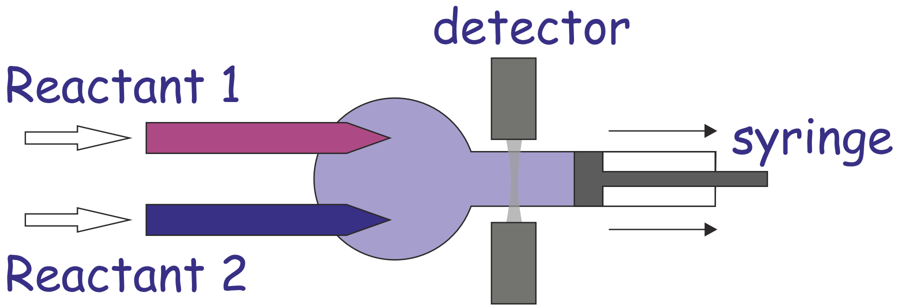
- A variation on the technique uses a fixed detector and a moveable injector for one of the reactants.

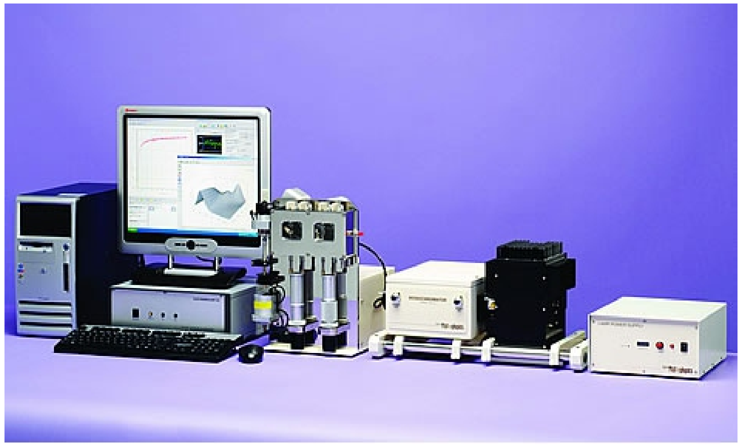


- Relatively large quantitites of reactants are required, and very high flow velocities are needed to study fast reactions.

Techniques for mixing reactants and initiating reaction

Stopped flow techniques





- Fixed volumes of reactants are rapidly mixed and flowed into a reaction chamber by a syringe fitted with an end stop.

- Reaction mixture composition is monitored spectroscopically as a function of time with a fixed detector.

- Very small sample volumes make stopped flow techniques suitable for studying biochemical reactions e.g. enzyme action.

- All flow techniques may suffer complications arising from heterogeneous reactions occurring at the flow tube surface.
    - minimise by coating flow tube with teflon or halocarbon wax (inert)
    - quantify by varying flow tube diameter (changes ratio of volume to surface area)

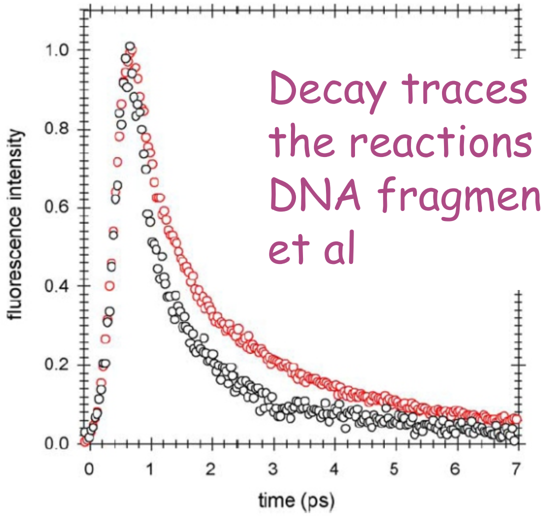
Techniques for mixing reactants and initiating reaction

Flash photolysis

- A pulse of light dissociates a precursor in the reaction mixture to produce a reactive species and initiate reaction.

$$AX + h\nu \rightarrow A + X$$
$$A + B \rightarrow \text{products}$$

- The concentration of the reactive species is monitored as a function of time after initiation, usually spectroscopically via absorption or fluorescence.



Decay traces from a study of the reactions of photoexcited DNA fragments by Markovitsi et al

Advantages

- Reactants produced from well mixed precursors, so no mixing time to reduce time resolution.

- Reactants generated and monitored in centre of reaction cell, so no problems arising from wall reactions.

Techniques for mixing reactants and initiating reaction

Laser pump-probe techniques

- A variation on flash photolysis used to study very fast processes.
- Pulsed lasers are used both to initiate reaction (the ‘pump’) and detect products via a pulsed spectroscopic technique (the’probe’).
- The time delay between the two lasers is varied electronically or optically, with delays as short as around 10 fs possible.

Speed of light = 2.997 x 10^8 ms^{-1}
Each metre travelled provides an optical delay of around 3 ns.

Summary of last lecture

Definitions

Elementary reaction

Chemical process occurring in a single step, may be unimolecular, bimolecular, or termolecular.

Complex reaction

A reaction comprising a sequence of elementary steps.

Reaction rate

Rate of change of a reactant or product with time (corrected for reactant stoichiometry)

Rate law

Expression relating the rate of reaction to the concentrations of species appearing in the reaction equation. May be 'simple' or 'complex'.

Integrated rate law

Expression relating reactant concentrations to the time elapsed since the reaction was initiated.

Half life

Time taken for the concentration of a reactant not present in excess at the start of the reaction to fall to half of its initial value.

Summary of last lecture

How do we measure the rate of a chemical reaction?

1. Mix the reactants and initiate reaction on a timescale that is negligible relative to that of the reaction.

2. Monitor the concentration(s) of one or more reactants and/or products as a function of time.

3. Since rate constants change with temperature, the temperature must be accurately measured and controlled.

Techniques for mixing reactants and initiating reaction

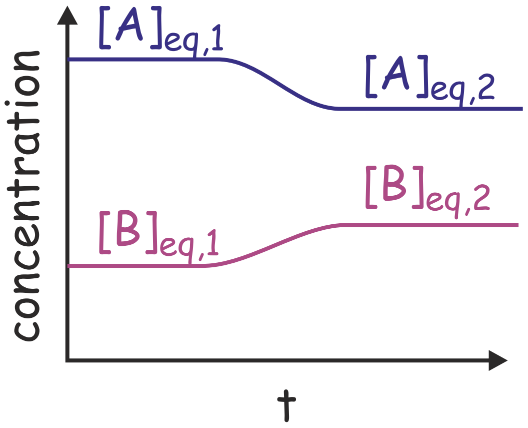
Relaxation methods

- If we perturb a system at equilibrium, the rate of relaxation to a new equilibrium depends on the rate constants for the forward and reverse reactions.

  Advantage: a system at equilibrium is already well mixed.

- The perturbation is often a 'temperature jump' of a few degrees achieved by
  - discharging a high voltage capacitor through the solution (~10^{-7} s)
  - a UV or IR laser pulse
  - a microwave discharge

Example: Consider a simple equilibrium at a temperature T_1.



$$A \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} B$$

rate constant for forwards reaction

rate constant for reverse reaction

Techniques for mixing reactants and initiating reaction

Relaxation methods

$$A \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} B \qquad \frac{d[A]}{dt} = -k_{1f}[A] + k_{1r}[B]$$

rate of change of [A]

- At equilibrium, [A] is constant, so

$$k_{1f}[A]_{eq,1} = k_{1r}[B]_{eq,1}$$

- Now apply temperature jump and allow concentrations to relax from $[A]_{eq,1}$ and $[B]_{eq,1}$ to new equilibrium concentrations $[A]_{eq,2}$ and $[B]_{eq,2}$, given by

$$k_{2f}[A]_{eq,2} = k_{2r}[B]_{eq,2}$$

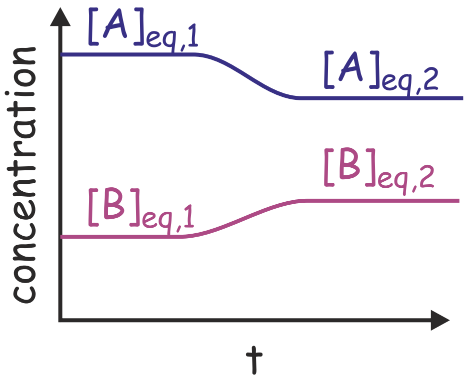
Note: new higher T rate constants k_{2f} and k_{2r}

- Define the deviation of the concentration from the new equilibrium values.

$$[A] - [A]_{eq,2} = x \quad \text{and} \quad [B] - [B]_{eq,2} = -x$$

- During the relaxation our concentrations are therefore

$$[A] = [A]_{eq,2} + x \quad \text{and} \quad [B] = [B]_{eq,2} - x$$



Techniques for mixing reactants and initiating reaction

Relaxation methods

$$A \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} B \qquad [A] = [A]_{eq,2} + x \quad \text{and} \quad [B] = [B]_{eq,2} - x$$

- During the relaxation, the rate of change of the concentrations is therefore

$$\frac{d[A]}{dt} = -k_{2f}[A] + k_{2r}[B]$$

$$= -k_{2f}([A]_{eq,2} + x) + k_{2r}([B]_{eq,2} - x) \qquad \text{but } k_{2f}[A]_{eq,2} = k_{2r}[B]_{eq,2}$$

$$\frac{dx}{dt} = -(k_{2f} + k_{2r})\,x$$

Relaxation rate is first order and depends on sum of rate constants for forward and reverse reactions

- Integrating gives

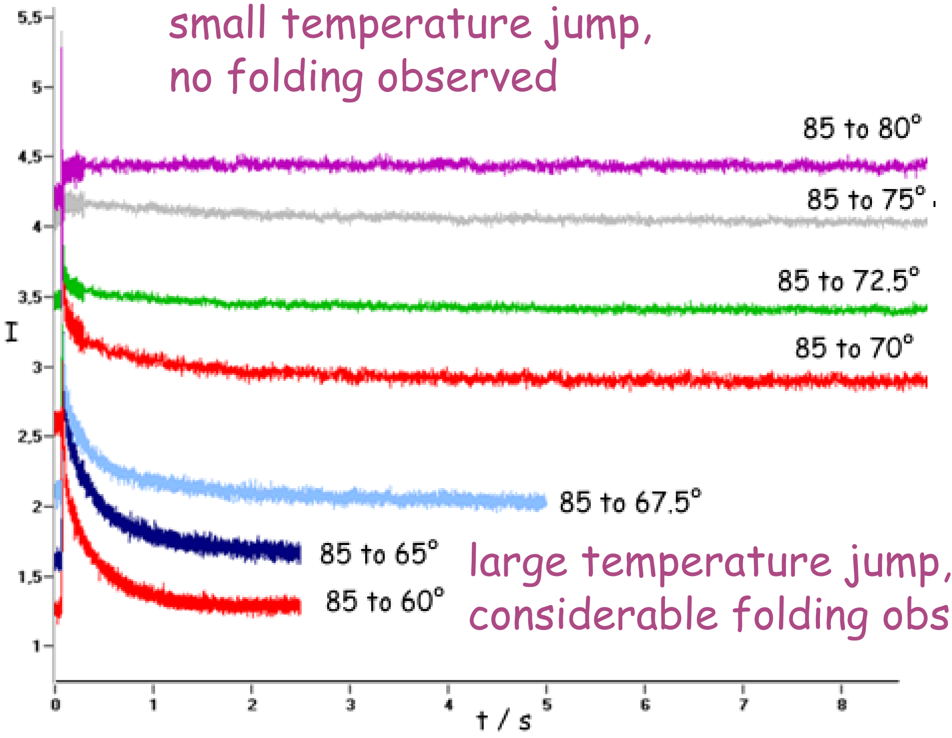
$$x = x_0 \exp(-t/\tau) \qquad \text{with} \qquad \frac{1}{\tau} = k_{2f} + k_{2r}$$

- Relaxation rate constant is $k = k_{2f} + k_{2r}$ and new equilibrium constant is $K = k_{2f}/k_{2r}$, so measuring both allows k_{2f} and k_{2r} to be found.

- Different reactions yield different equations, but the basic principle is the same.

Techniques for mixing reactants and initiating reaction

Relaxation methods - an example

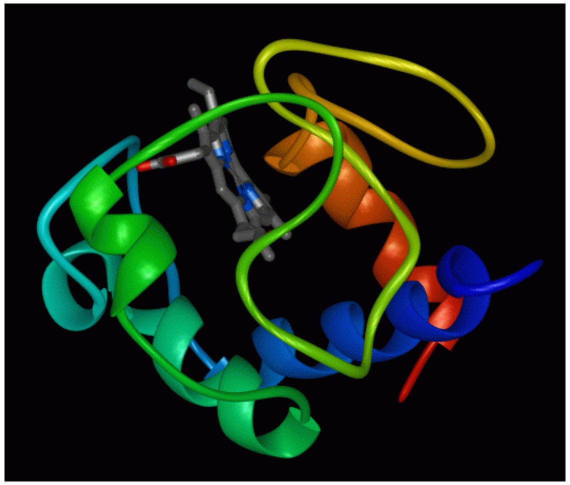


small temperature jump, no folding observed

large temperature jump, considerable folding observed

Experiments carried out at BioLogic Science Instruments

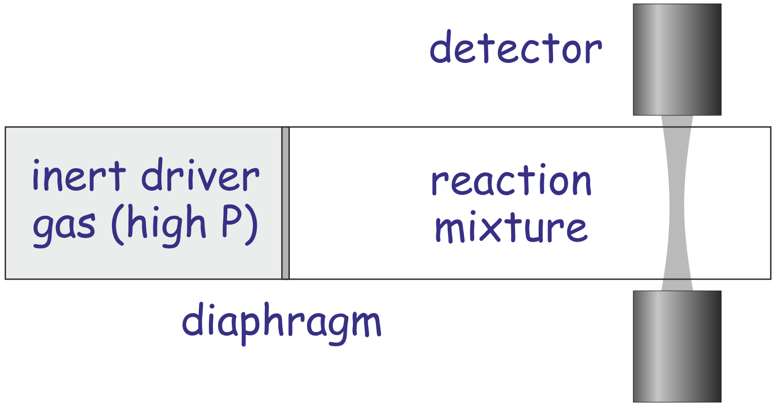
- Refolding of denatured cytochrome-c following a 'cold jump' (temperature reduced suddenly by adding cold buffer solution)
- Monitored through laser-induced fluorescence of tryptophan residues in the protein.

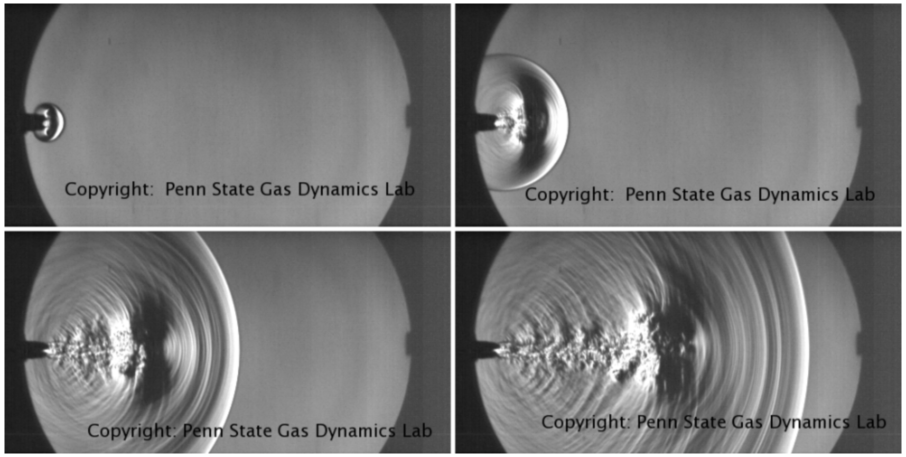


Techniques for mixing reactants and initiating reaction

Shock tubes

- An alternative to discharges and laser pulses for producing reactive species through dissociation of a molecular precursor.





shock wave leaving the end of an open shock tube

- Puncturing the diaphragm leads to a very rapid increase in pressure and rapid heating of the reaction mixture to several thousand Kelvin.
- Leads to rapid production of reactive species through dissociation of precursor molecules, initiating the reaction of interest.
- Temperature rise can be controlled by varying pressure and composition of inert gas.

Techniques for mixing reactants and initiating reaction

Shock tubes

- Often used to study combustion reactions. Suitable precursors include:

$HCN \rightarrow H + CN$

$SO_2 \rightarrow SO + O$

$CH_3 \rightarrow CH_2 + H$

$H_2S \rightarrow HS + H$

$NO \rightarrow N + O$

$NH_3 \rightarrow NH_2 + H$

$CH_4 \rightarrow CH_3 + H$

$N_2O \rightarrow N_2 + O$

$C_2H_2 \rightarrow C_2H \ \_ \ H$

$CF_3Cl \rightarrow CF_3 + Cl$

$C_2H_4 \rightarrow C_2H_3 + H$

$C_2H_4 \rightarrow C_2H_2 + H_2$

Drawbacks:

- Not very selective!
  ⇒ complicated mixture of reactive species and a large number of extra reactions occurring, difficult to model.

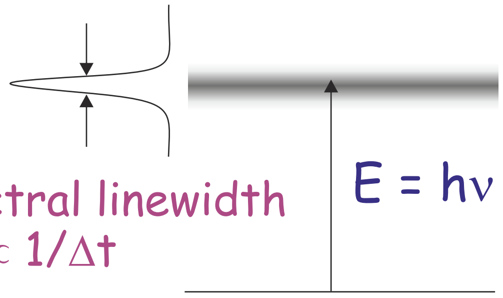
- Each experiment is a ‘one off’ so no signal averaging is possible.

Techniques for mixing reactants and initiating reaction

Lifetime methods (kinetics of excited states)

- The Heisenberg uncertainty principle relates measurement uncertainties in position and momentum, and in energy and time.

$$\Delta x \, \Delta p \geq \frac{h}{4\pi} \qquad \Delta E \, \Delta t \geq \frac{h}{4\pi}$$



excited state
(lifetime = Δt)

$E = h\nu$

spectral linewidth
$\Delta E \propto 1/\Delta t$

ground state
(lifetime = ∞)

- An electronic state has an energy uncertainty related to its lifetime.
- A spectral line therefore has a finite width known as the natural linewidth.

- Kinetic processes involving an excited state reduce its lifetime (for first order processes $k = 1/\Delta t$) and broaden spectral lines further.
- Rate constants may therefore be extracted from linewidths. Timescales range from ~10^{-15} s in photoelectron spectroscopy to ~1 s in NMR.

Techniques for monitoring concentrations as a function of time

Slow reactions

Real time analysis

- Composition of reaction mixture monitored while reaction is in progress by withdrawing a small sample or monitoring the bulk.

Quenching method

- Reaction is stopped a certain time after initiation and the composition analysed at leisure. e.g.
    - sudden cooling
    - drastic dilution
    - rapid neutralisation of an acidic reagent
    - removal of a catalyst
    - addition of a quencher

- The reaction must be slow enough/quenching fast enough that no significant reaction occurs during the quenching process.

- Real time and quenching methods are often combined by withdrawing and quenching small samples of reaction mixture at a series of times during the reaction.

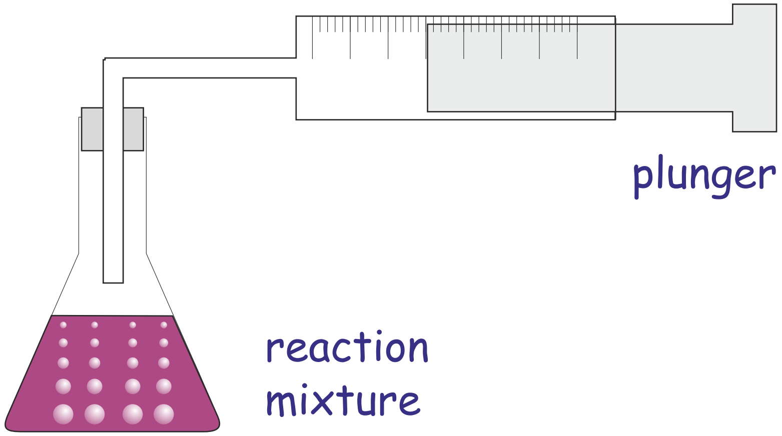
Techniques for monitoring concentrations as a function of time

Slow reactions

The reaction mixture composition may be followed by tracking any chemical or physical change that occurs as the reaction proceeds.

Examples

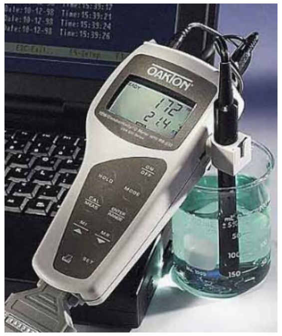
1. Reactions involving gases:
    - follow the pressure (at constant volume).
    - measure the volume of gas evolved (at constant pressure)
    - follow the change in mass of the system.



Techniques for monitoring concentrations as a function of time

Slow reactions

2. Reactions involving ions
   - conductivity or pH measurements



conductivity meter

pH meter

3. For very slow reactions, the mixture may be titrated to determine the concentrations of one or more components.

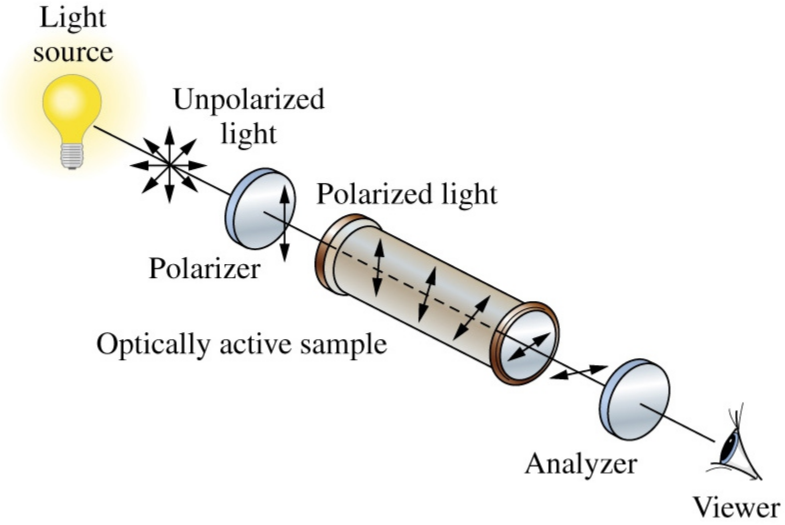
Techniques for monitoring concentrations as a function of time

Slow reactions

4. If one component is coloured then colourimetry is an option.

5. Absorption or emission spectroscopy (more later)

6. Reactions involving chiral compounds may be tracked using polarimetry (measurement of optical activity).



7. Other techniques - mass spectrometry, gas chromatography, NMR/ESR, and many more.

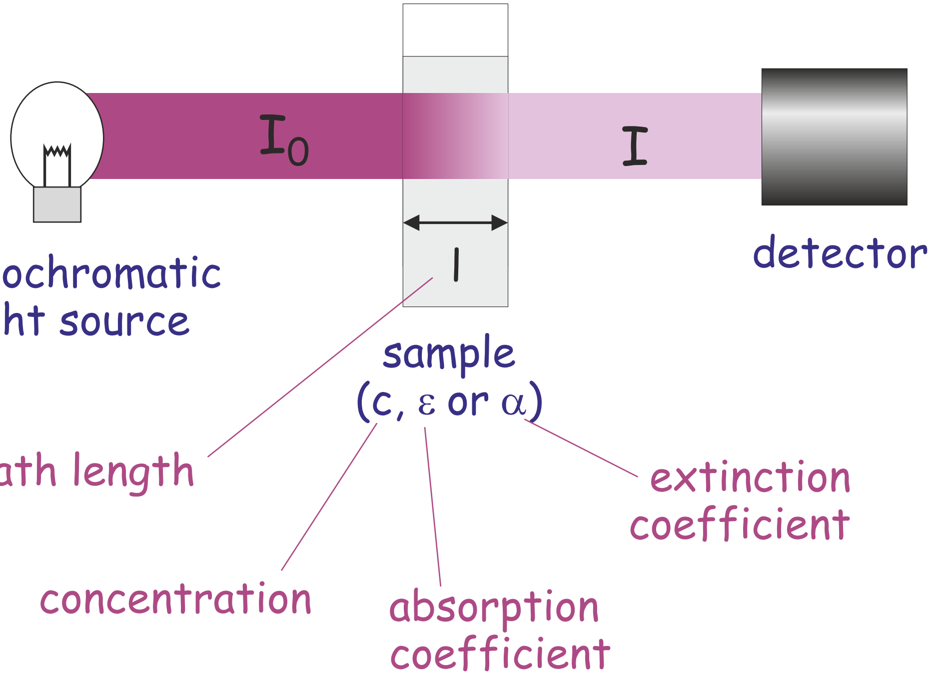
Techniques for monitoring concentrations as a function of time

Fast reactions

To monitor fast reactions we need a fast measurement technique. Most are based on some form of spectroscopy.

Absorption spectroscopy / spectrophotometry

- Can be used to track reactions when the reactants and products have different absorption spectra.



- Transmittance

$$T = \frac{I}{I_0} = 10^{-\varepsilon cl} \qquad T = \frac{I}{I_0} = e^{-\alpha cl}$$

or in log form

$$\log(I/I_0) = -\varepsilon cl \qquad \ln(I/I_0) = -\alpha cl$$

- Absorbance (optical density)

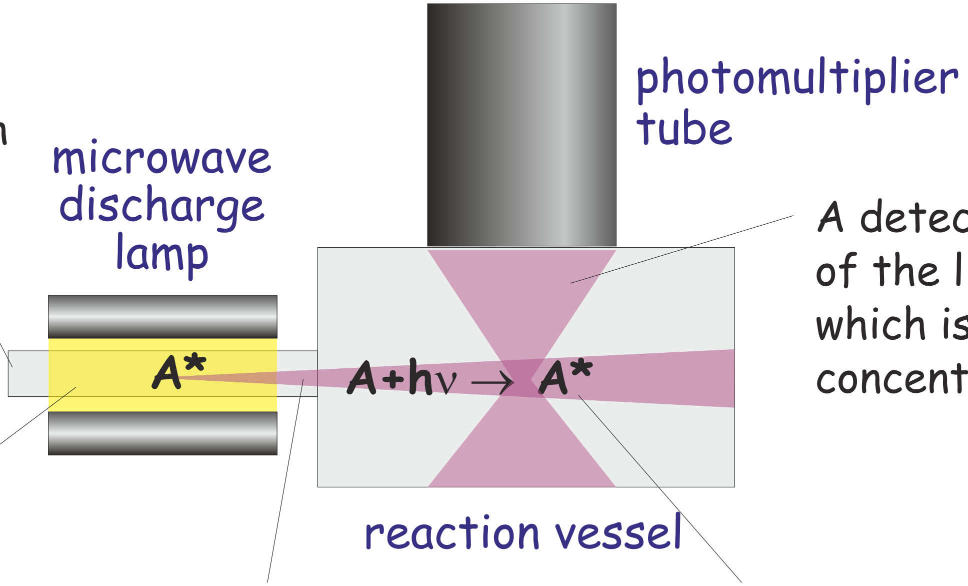
$$A = -\log T = \log(I/I_0) = \varepsilon cl$$

Techniques for monitoring concentrations as a function of time

Fast reactions

Resonance fluorescence

- Widely used for detecting atomic species e.g. H, N ,O, Br, Cl, F.



Discharge lamp filled with a mixture of He and a precursor for the atom of interest

The microwave discharge produces a mixture of ground and excited state atoms.

The lamp emits light at characteristic wavelengths as the excited state atoms emit photons and return to the ground state.

The light emitted by the lamp excites atoms of the same species in the reaction mixture.

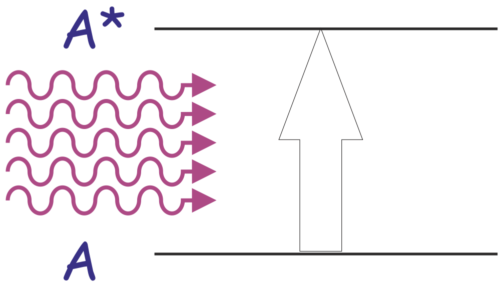
A detector records the intensity of the light emitted by these atoms, which is proportional to their concentration.

Techniques for monitoring concentrations as a function of time

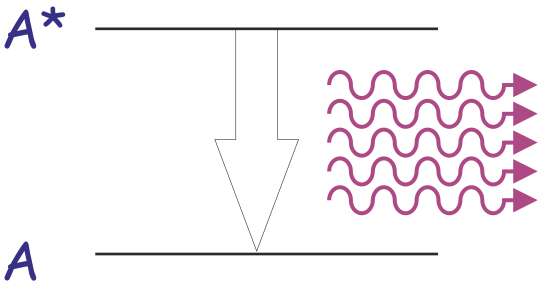
Fast reactions

Laser-induced fluorescence

- A laser is used to excite a chosen species in a reaction mixture to an electronically excited state.
- The excited state emits photons to return to the ground state, and the intensity of the fluorescent emission is measured.
- The number of excited state molecules produced by the laser pulse (and therefore the intensity of the emitted light) is proportional to the number/concentration of ground state molecules present in the reaction mixture.



laser excitation



emission and detection

Summary

We have looked at a range of methods for initiating chemical reactions and measuring their rates:

- Continuous flow techniques
- Stopped flow technique
- Flash photolysis / laser pump-probe
- Relaxation methods
- Shock tubes
- Lifetime methods / spectral line broadening (excited state kinetics)

Slow reactions - concentrations may be monitored either in real-time or after quenching by measuring any physical quantity that changes during the reaction e.g. pressure, pH, conductivity, colourimetry, titration etc

Fast reactions - concentrations are usually monitored using one of a number of spectroscopic techniques e.g. absorption spectroscopy, laser-induced fluorescence, resonance fluorescence.

Temperature control and measurement

- Rate constants are temperature dependent

$$k = A \exp(-E_a/RT)$$

pre-exponential factor

activation energy

- Consequences:

1. To measure an accurate value for k, the temperature of the reaction mixture must be maintained at a known, constant value.

2. To measure an activation energy, rate constants must be measured at a series of temperatures.

- The temperature is usually measured using a thermocouple (wide T range and measurement can be automated), but standard thermometers are also often used.

Temperature control

- Liquid phase reactions may be carried out inside a temperature-controlled thermostat.

- Gas phase reactions are usually carried out inside a stainless steel vacuum chamber, with thermal equilibrium maintained through collisions of the gas molecules with the chamber walls.

- High temperatures (up to 1300 K) may be obtained using standard resistive heaters.

- Low temperatures may be reached by flowing cooled liquid through the walls of the reaction vessel.

- Very low temperatures may be reached using cryogenic fluids such as liquid nitrogen (~ 77 K) or liquid helium (~ 4K).

- Extremely low temperatures may be obtained by preparing the reactants in a supersonic molecular beam (relevant to reactions in interstellar space).

What next?

- We have looked at a variety of ways in which to measure the rates of both slow and fast reactions.
- The data obtained in these experiments are the time-dependent concentrations of one or more reactants or products at one or more temperatures.
- Now we need to learn how to extract useful information from the data i.e. reaction orders, rate laws and rate constants.

Determining the rate law from experimental data

How do we extract reaction orders and rate laws from the rate data we have measured?

1. Isolation method

- A technique for simplifying the rate law in order to determine the dependence of the rate on the concentration of a single reactant.
- Once the rate law has been simplified, the differential or integral methods (next slide) allow us to determine the reaction orders.
- The dependence of the rate on the concentration of one reactant is isolated by having all other reactants present in large excess.

Example $A + B \rightarrow P$ $\quad \nu = k[A]^a[B]^b$

Now only one order needs to be extracted from the experimental data

With B in large excess, this becomes

$$\nu \approx k[A]^a[B]_0^b = k_{eff}[A]^a \quad \text{with} \quad k_{eff} = k[B]_0^b$$

- When the rate law contains several concentrations, a series of experiments may be carried out to isolate each reactant in turn.

1. Isolation method (contd...) - the 'pseudo order' terminology

The kinetics of reactions studied using the isolation method are often described in terms of 'pseudo orders'.

e.g. Consider a second order reaction with rate law

$$\nu = k[A][B]$$

If B is present in large excess, this becomes

$\nu \approx k[A][B]_0 = k_{eff}[A]$ with $k_{eff} = k[B]_0$

This is a first order rate law, and so we say that under these conditions the reaction is pseudo first order.

Determining the rate law from experimental data

2. Differential methods

- When the rate law only depends on one species (either because only one species is involved in the reaction or because we have used the isolation method) then

$$\nu = k[A]^a$$

$$\log \nu = \log k + a\log[A]$$

- A plot of $\log\nu$ against $\log[A]$ is a straight line with a slope equal to the order a and an intercept equal to log k

- Data to plot may be obtained in two ways:

1. Measure [A] as a function of time and use the data to determine the rate, $\nu = d[A]/dt$ as a function of [A]. i.e. obtain required data in a single expt.

2. Make a series of measurements of the initial rate of the reaction, ν_0, with different initial concentrations, $[A]_0$. This is a common technique known as the initial rates method. i.e. obtain required data from a series of expts.

Determining the rate law from experimental data

3. Integral methods

- Once we have measured concentrations as a function of time, we can compare their time dependence with the appropriate integrated rate laws.

- If we have used the isolation method so that the rate law only depends on one reactant concentration, only fairly simple integrated rate laws are required, depending on the value of the order, a.

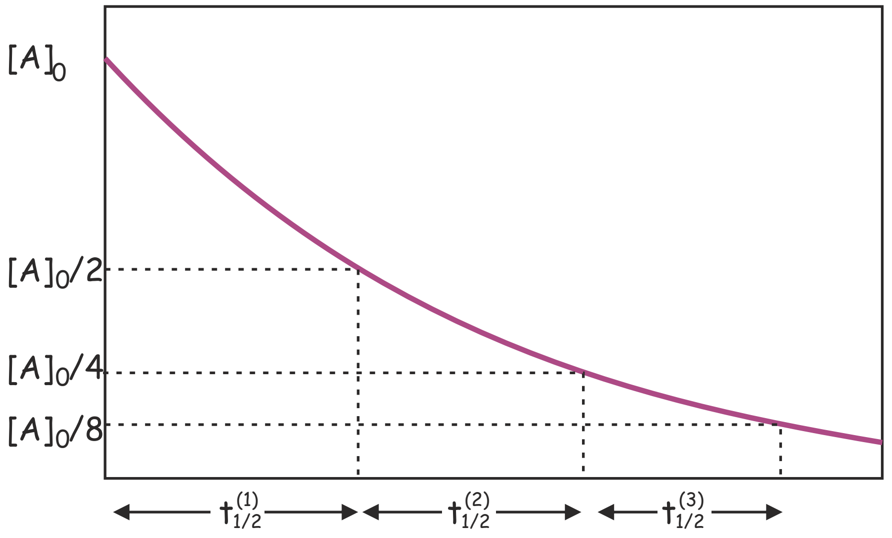
zeroth order	$[A] = [A]_0 - kt$	A plot of $[A]$ vs t is linear, with slope -k.
first order	$\ln[A] = \ln[A]_0 - kt$	A plot of $\ln[A]$ vs t is linear, with slope -k.
second order	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$	A plot of $1/[A]$ vs t is linear, with slope 2k.

- If none of these plots yield a straight line then more complicated rate laws must be investigated.

Determining the rate law from experimental data

4. Half lives

Another option is to measure a series of half lives for the reaction and compare the observed values with the known behaviour for various reaction orders.



zeroth order $t_{1/2} = \dfrac{[A]_0}{2k}$

After one half life has elapsed, the new starting concentration is $[A]_0/2$, so successive half lives decrease by a factor of two

first order $t_{1/2} = \dfrac{\ln 2}{k}$

The half life has no concentration dependence, so successive half lives are identical.

second order $t_{1/2} = \dfrac{1}{k[A]_0}$

Inverse dependence on concentration, so successive half lives double.

Recap and forward look

- We have looked at a variety of ways to follow changing concentrations and measure reaction rates for slow and fast reactions.

- We have considered how to use the experimental data to determine the orders with respect to each reactant.

- Now we need to look at kinetic mechanisms (sequences of elementary steps) in more detail and learn how to use a proposed mechanism to obtain a rate law for comparison with experiment.

- We will look at a range of examples of different types of reactions and their rate laws:

consecutive/sequential elementary reactions
competing elementary reactions
pre-equilibria
"unimolecular" reactions
third order reactions
enzyme reactions
chain reactions
explosions

Kinetic mechanisms and rate laws

- A kinetic mechanism may be used to predict a rate law.

- Disagreement of a predicted rate law with experimental data rules out the proposed mechanism.

- Agreement of a predicted rate law with experimental data inspires some confidence in the mechanism, BUT

- A proposed mechanism must also account for all other properties of the reaction:
    - product distribution
    - product stereochemistry
    - kinetic isotope effects
    - temperature dependence
    - etc

- Any mechanism involving more than one elementary step is referred to as a complex mechanism.

Consecutive reactions

- The simplest complex reaction consists of two consecutive, irreversible elementary steps.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- An example is radioactive decay.

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He \rightarrow {}^{234}_{91}Pa + e^-$$

- This is one of the few cases in which we can solve the rate equations analytically to find the concentrations of A, B and C as a function of time.

$$\frac{d[A]}{dt} = -k_1[A]$$

At t = 0 $[A] = [A]_0$
$[B] = [C] = 0$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

At all times $[A] + [B] + [C] = [A]_0$

$$\frac{d[C]}{dt} = -k_2[B]$$

Consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(1) $$\frac{d[A]}{dt} = - k_1[A]$$

(2) $$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

(3) $$\frac{d[C]}{dt} = - k_2[B]$$

At t = 0 $[A] = [A]_0$
$[B] = [C] = 0$

At all times $[A] + [B] + [C] = [A]_0$

- We can integrate (1) directly to give $[A] = [A]_0\exp(-k_1t)$.
- Substituting this result into (2) gives a differential equation in [B]

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 \exp(-k_1t)$$

with the solution

$$[B] = \frac{k_1}{k_2-k_1}\{\exp(-k_1t) - \exp(-k_2t)\} [A]_0$$

- Finally, since $[C] = [A]_0 - [A] - [B]$, we have

$$[C] = \left(1 + \frac{k_1\exp(-k_2t) - k_2\exp(-k_1t)}{k_2-k_1}\right) [A]_0$$

Prove these results if you'd like some maths practice!

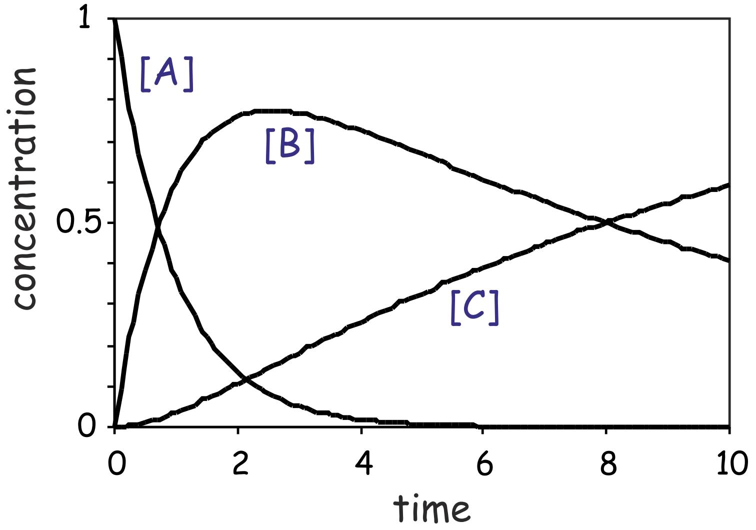
Consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

$$[C] = \left(1 + \frac{k_1\exp(-k_2t) - k_2\exp(-k_1t)}{k_2-k_1}\right)[A]_0$$

- Consider the two cases in which $k_1 \gg k_2$ and $k_2 \gg k_1$.

$k_1 \gg k_2$

$(k_1 = 1, k_2 = 0.1)$



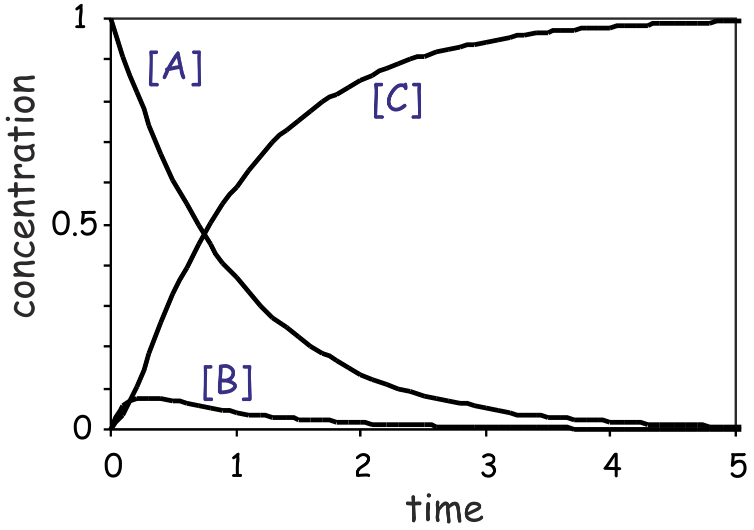
- All A initially present is rapidly converted into B, which is then used up slowly to form C.
- Formation of C follows the rate law

$$[C] = \{1 - \exp(-k_2t)\}\,[A]_0$$

- Apart from at the very start of the reaction, the overall rate is independent of k_1; step 2 is the rate determining step.

$k_2 \gg k_1$

$(k_1 = 1, k_2 = 10)$



- B is consumed as soon as it is produced.
- Formation of C follows the rate law

$$[C] = \{1 - \exp(-k_1t)\}\,[A]_0$$

- The overall rate now depends only on k_1, and the first step is rate determining.

Pre-equilibria

- Consider a reaction system only slightly more complicated than that of consecutive irreversible reactions, in which the first reaction is now reversible.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_2} D$$

- The rate equations are now

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_{-1}[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[C]$$

$$\frac{d[D]}{dt} = k_2[C]$$

- These cannot be solved analytically, and in general must be integrated numerically.

- However, if $k_{-1} \gg k_2$, the situation is greatly simplified.

Pre-equilibria

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \overset{k_2}{\rightarrow} D$$

- If $k_{-1} >> k_2$, an equilibrium is reached between the reactants A and B and the intermediate C. The equilibrium is only slightly perturbed by C 'leaking' away to form the product D.

- To a very good approximation, once the equilibrium has been established, the rates of the forward and reverse reaction must be equal.

$$k_1[A][B] = k_{-1}[C]$$

- We can rearrange this to obtain

$$\frac{k_1}{k_{-1}} = \frac{[C]}{[A][B]} = K$$

equilibrium constant is equal to the ratio of the rate constants for the forward and reverse reactions.

- The overall rate (rate of formation of D) is then

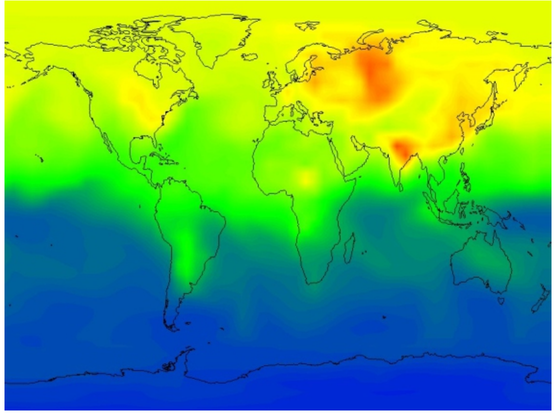
$$\nu = \frac{d[D]}{dt} = k_2[C] = k_2K[A][B]$$

Second order kinetics, with effective rate constant
$k_{eff} = k_2K$

- Only holds once equilibrium has been established i.e. not in early stages of reaction

More complicated mechanisms

- We have looked at two simple examples in which the rate equations may be solved exactly (or approximately exactly, in the case of pre-equilibria).
- In general, rate equations for a reaction represent a complicated system of coupled differential equations, which cannot be solved analytically.



Global CH_4 concentrations

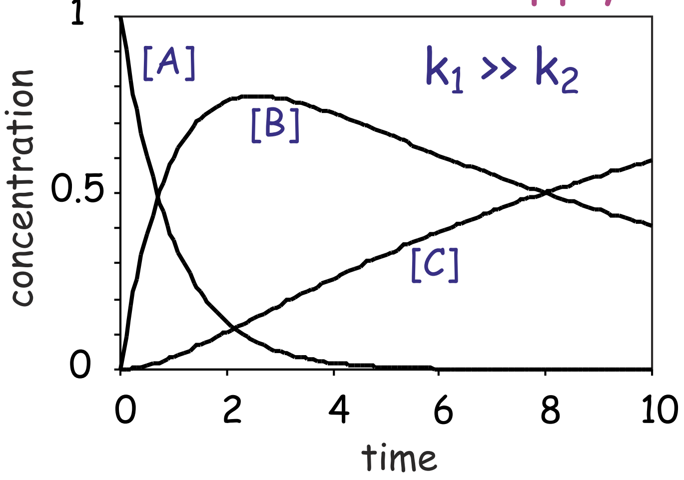
e.g. atmospheric modelling - many hundreds or even thousands of interdependent reactions. Rate laws must be integrated numerically to determine time-dependent concentrations of atmospheric constituents.

- Luckily, approximate solutions may be obtained by making a few simple assumptions about the nature of reactive intermediates

The steady state approximation

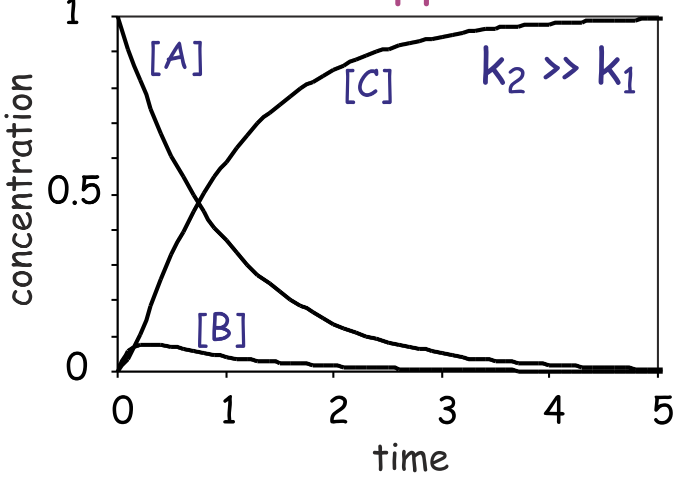
- A reactive intermediate R is used up virtually as soon as it is formed, so its concentration will remain low and essentially constant throughout the course of the reaction (apart from at the very beginning and end of the reaction).

- To a good approximation, we can therefore set d[R]/dt = 0 in the rate equations.



SSA does not apply

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$



SSA applies

Coupled differential
rate equations

⇒ SSA

Simultaneous algebraic
rate equations

Cannot be solved analytically

Can be solved analytically

The steady state approximation - example

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \overset{k_2}{\rightarrow} D \qquad k_2 >> k_1, k_{-1}$$

- Same reaction as in the pre-equilibrium case, but C is now a reactive intermediate and there is no stable equilibrium between A, B and C.

- Applying the SSA to C gives

$$\frac{d[C]}{dt} = 0 = k_1[A][B] - k_{-1}[C] - k_2[C] \qquad \text{so} \qquad [C] = \frac{k_1}{k_{-1}+k_2}[A][B]$$

- The overall rate is therefore

$$\nu = \frac{d[D]}{dt} = k_2[C] = \frac{k_1k_2}{k_{-1}+k_2}[A][B]$$

- Note that if $k_2 >> k_{-1}$ then, not surprisingly, the overall rate is the same as the rate of the first, rate determining step

The steady state approximation - "recipe"

1. Write down a steady state equation for each reactive intermediate

2. Solve the equations to obtain expressions for the steady state concentrations of each intermediate.

   (i) If the equation only contains one reactive intermediate, simply rearrange to obtain the concentration. This can then often be substituted into one or more of the remaining equations to find the rate law.

   (ii) If the equations depend on more than one intermediate and share terms, look for sums and/or differences of equations that will simplify them (equations that at first sight look extremely complicated often become trivial when you add two of them together)

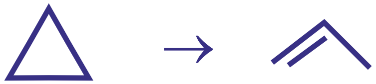
3. Write down an expression for the overall rate (usually the rate of change of one of the products). This will generally depend on reactive intermediates.

4. Substitute your results from step 2 into the overall rate equation and simplify to obtain an overall rate equation that depends only on reactant and product concentrations.

   Concentrations of reactive intermediates must not appear in the final rate law.

‘Unimolecular reactions’ - the Lindemann-Hinshelwood mechanism

- A number of gas-phase reactions follow first order kinetics and only appear to involve one reactant.



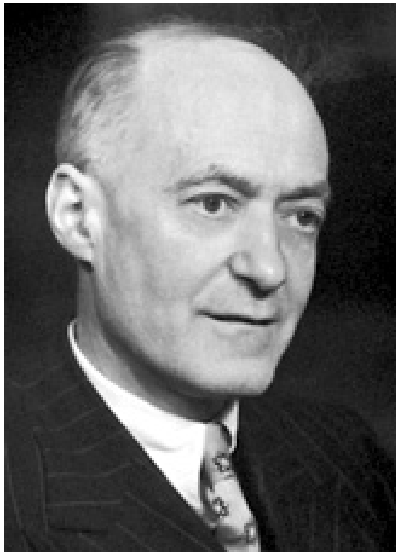
isomerisation of cyclopropane

$CH_3N_2CH_3 \rightarrow C_2H_6 + N_2$

decomposition of azomethane

- How do the reactants acquire enough energy to react?

- Solved by Lindemann in 1922, and “polished” by Hinshelwood.



Sir Cyril Hinshelwood

Nobel Prize Winner 1956

“for his researches into the mechanism of chemical reactions”

and PTCL head of department!

'Unimolecular reactions' - the Lindemann-Hinshelwood mechanism

- How do the reactants acquire enough energy to react?

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

A acquires energy by colliding with another molecule, M (which might be another A).

$$A^* \xrightarrow{k_2} P$$

The excited reactant A* then undergoes unimolecular reaction to form products.

- We can apply the SSA to the excited state A*

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

and rearrange to find the concentration of A*.

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

- The overall rate law is therefore

$$\nu = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_1k_2[A][M]}{k_{-1}[M] + k_2}$$

'Unimolecular reactions' - the Lindemann-Hinshelwood mechanism

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \overset{k_2}{\rightarrow} P$$

$$\nu = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

A first order rate law ?!

- Consider the high and low pressure limits:

High pressure - Many collisions, so collisional de-excitation of A^* is much more likely than unimolecular reaction to form products.

$$\nu = \frac{k_1 k_2}{k_{-1}} [A]$$

First order with effective rate constant $k_{uni} = k_1 k_2 / k_{-1}$.

Explains experimental observations

Low pressure - Few collisions, so unimolecular reaction of A^* is much more likely than collisional de-excitation.

$$\nu = k_1 [A][M]$$

Second order kinetics because formation of A^* is now the rate determining step.

Testing the Lindemann-Hinshelwood mechanism

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

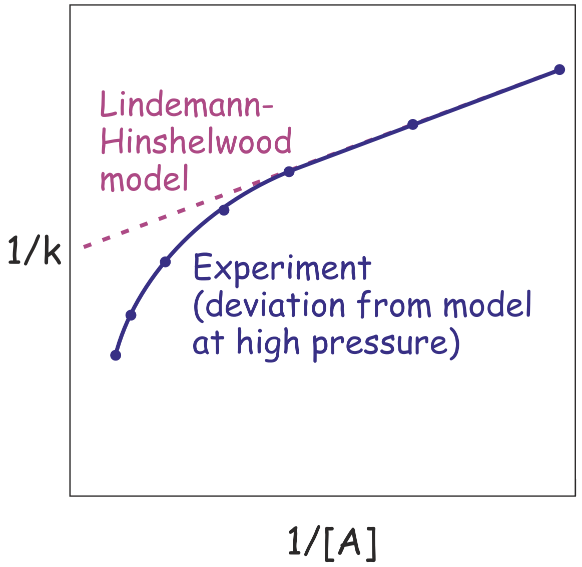
$$A^* \xrightarrow{k_2} P$$

$$\nu = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

- Rewrite in the form of a first order rate law.

$$\nu = k[A] \qquad \text{with} \qquad k = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2} \quad \Rightarrow \quad \frac{1}{k} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [M]}$$

- A plot of 1/k vs 1/[M] should be linear, with a slope of $1/k_1$ and an intercept of $k_{-1}/(k_1 k_2)$



- Reasonable fit at low pressure, but large deviations at high pressure (rate constant larger than predicted)
- Lindemann-Hinshelwood mechanism assumes that any excited state A* can undergo unimolecular reaction.
- Usually excitation is needed in a particular degree of freedom (e.g. vibration of a bond that breaks in the reaction).
- More sophisticated theories take this into account.

Summary of last lecture

- We started to consider complex reaction mechanisms and their rate laws.

1. Simplest complex mechanism - consecutive irreversible reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- Rate equations may be solved exactly.
- Considered the two limiting cases of $k_1 \gg k_2$ and $k_2 \gg k_1$, and showed that the rate laws then depended only on k_1 or k_2 i.e. there is a rate-determining step.

2. Slightly more complicated mechanism.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_2} D$$

- Rate equations can no longer be solved exactly.
- In the case where $k_2 \ll k_1, k_{-1}$, we have a pre-equilibrium, and we can use the equilibrium constant to find [C], and therefore the overall rate law.

$$\nu = \frac{d[D]}{dt} = k_2[C] = k_2K[A][B]$$

Summary of last lecture

1. We introduced the steady state approximation (SSA):

   - Assume that all reactive intermediates R are present in low and constant concentration over most of the course of the reaction, such that $d[R]/dt = 0$.

   - This transforms the complicated coupled differential rate equations into a set of algebraic equations, which are relatively straightforward to solve.

2. We applied the steady state approximation to the derivation of overall rate laws for 'unimolecular' reactions (Lindemann-Hinshelwood mechanism)

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

$$\nu = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

Third order reactions

- A number of reactions are found to have third order kinetics e.g.

$$2NO + O_2 \rightarrow 2NO_2 \qquad \frac{d[NO_2]}{dt} = k\,[NO]^2[O_2]$$

- This is not an elementary process:
  - Three body collisions are far too unlikely to explain the observed reaction rate.
  - The rate decreases with increasing temperature, indicating a complex mechanism.
- An alternative mechanism involves a pre-equilibrium.

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NO)_2$$

$$(NO)_2 + O_2 \xrightarrow{k_2} 2NO_2$$

$$\nu = \frac{1}{2}\frac{d[NO_2]}{dt} = k_2[(NO)_2][O_2]$$

- From the pre-equilibrium, we have

$$K = \frac{[(NO)_2]}{[NO]^2} \quad \text{and} \quad [(NO)_2] = K[NO]^2$$

- The overall rate is therefore

$$\nu = k_2K\,[NO]^2[O_2]$$

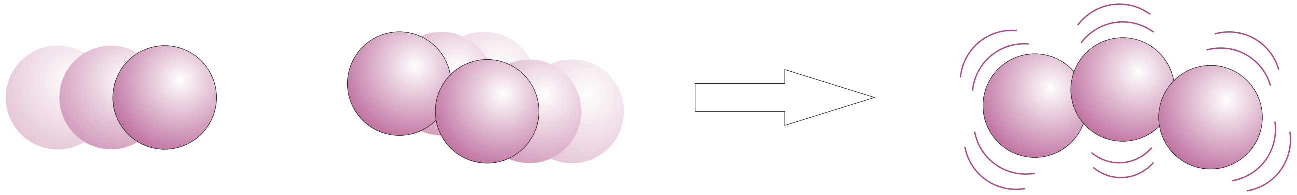
Third order, as required

Third order reactions

- A common class of third order reactions are those in which two reactants combine to form a single product. Consider:

$$O + O_2 \rightarrow O_3$$

- As written, this reaction would barely occur due to the consequences of conservation of energy and momentum.



Conservation of momentum means that the collision energy and reaction exothermicity goes into internal excitation of the O_3 product.

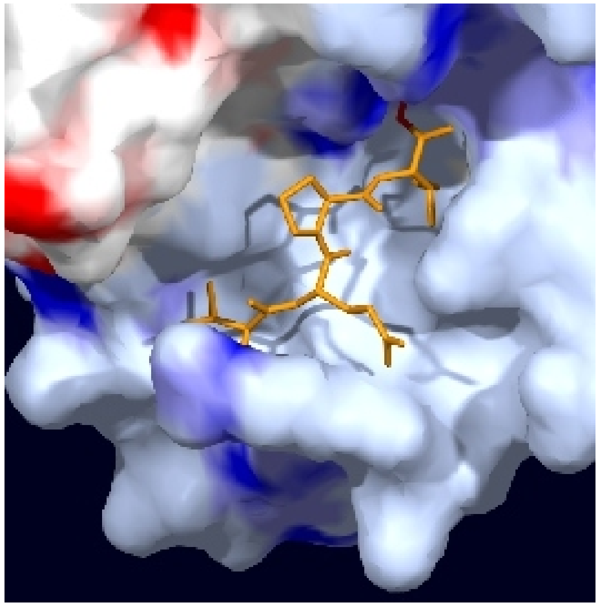
- The only way for the vibrationally excited O_3 to survive is to transfer some of its energy to another molecule (a 'third body') in a collision.

$$O + O_2 \rightleftharpoons O_3^*$$
$$O_3^* + M \rightarrow O_3 + M$$

Usually written $O + O_2 + M \rightarrow O_3 + M$

- Note that if two or more products are formed the energy can be carried away as product relative translation and no third body is required.

Enzyme reactions - background



- An enzyme is a protein that catalyses a specific (bio)chemical reaction by lowering the activation energy.

- The reactant molecule (the substrate) binds to the active site on the enzyme.

- Binding shifts the substrate geometry closer to that of the transition state for the reaction, lowering the activation energy.

- Enzyme-catalysed reactions are millions of times faster than uncatalyzed reactions, and virtually every chemical reaction in biology requires an enzyme in order to occur at a significant rate.

- Many drugs work by binding to a carefully targeted enzyme in place of the normal substrate, thereby blocking its action.

Enzyme reactions - experimental data

Any kinetic model for enzyme action must explain the following:

- For many enzyme reactions, the rate is found to follow the Michaelis-Menten equation.

maximum rate

substrate concentration

$$\nu = \frac{\nu_{max}[S]}{K_M+[S]}$$

Michaelis constant

- The maximum rate is found to be proportional to the total concentration of enzyme, [E], even though there is no net change in this quantity over the course of the reaction.

$$\nu_{max} = k_{cat}[E]_0$$

'turnover number' - maximum number of substrate molecules that each enzyme can convert into products per second

Enzyme reactions - trial mechanism

Try a very simple trial mechanism.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$$

E = enzyme
S = substrate
ES = enzyme-substrate complex
P = product

Can we use the steady state approximation?

- [ES] is not much less than the reactant concentration [E], so we may think not...
- ....but, because [E] is regenerated in the second step, both [E] and [ES] change much more slowly than [S] and [P], so the SSA is valid and we can apply it to [ES].

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES] \quad \Longrightarrow \quad [ES] = \frac{k_1[E][S]}{k_{-1}+k_2}$$

- The total enzyme concentration is $[E]_0 = [E] + [ES]$, so $[E] = [E]_0 - [ES]$.

$$[ES] = \frac{k_1([E]_0-[ES])[S]}{k_{-1}+k_2} \quad \Longrightarrow \quad [ES] = \frac{k_1[E]_0[S]}{k_{-1}+k_2+k_1[S]}$$

Enzyme reactions - trial mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\rightarrow} P + E \qquad [ES] = \frac{k_1[E]_0[S]}{k_{-1}+k_2+k_1[S]}$$

- The overall rate of formation of products is then

$$\nu = \frac{d[P]}{dt} = k_2[ES] = \frac{k_2k_1[E]_0[S]}{k_{-1}+k_2+k_1[S]}$$

- If we define

$$K_M = \frac{k_2+k_{-1}}{k_1}$$

then we can write the rate as

$$\nu = \frac{k_2[S][E]_0}{K_M+[S]} = k\,[E]_0 \qquad \text{with} \qquad k = \frac{k_2[S]}{K_M+[S]}$$

- Our mechanism predicts the Michaelis-Menten equation, with $k_2 = k_{cat}$.

Enzyme reactions - analysis of the Michaelis-Menten equation

$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\rightarrow} P + E$ $\nu = \frac{k_2[S][E]_0}{K_M+[S]} = k\,[E]_0$ with $k = \frac{k_2[S]}{K_M+[S]}$

- Rate of enyzyme-catalysed reaction depends linearly on [E], and in a more complicated way on [S]. This dependence simplifies in two cases:

1. $[S] \ll K_M$

   - The rate is $\nu = (k_2/K_M)[E]_0[S]$, and the rate is first order in both [E] and [S].

2. $[S] \gg K_M$

   - The rate is $\nu = k_2[E]_0 = k_{cat}[E]_0$ and is independent of [S]

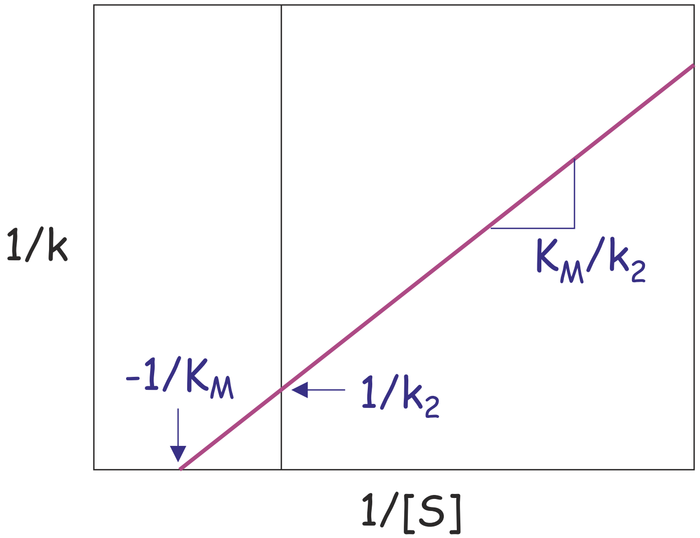
   - There is so much substrate present that [S] is essentially constant, the enzyme is saturated with substrate and the rate is a maximum, $\nu = \nu_{max}$.

Enzyme reactions - rate constants from experimental data

- We can rewrite our expression for the rate constant by inverting it.

$$k = \frac{k_2[S]}{K_M+[S]} \quad \Rightarrow \quad \frac{1}{k} = \frac{K_M}{k_2[S]} + \frac{1}{k_2}$$

- A plot of 1/k against 1/[S] (a Lineweaver-Burke plot) has a slope of K_M/k_2 and an intercept of $1/k_2$.



- Usually use the initial rates method to measure k to prevent complications due to secondary reactions of the products.

Chain reactions

- Chain reactions contain chain carriers - reactive intermediates that react to form further reactive intermediates.

  e.g. destruction of ozone by CFCs

$C_nF_mCl + h\nu \rightarrow \cdot C_nF_m + \cdot Cl$

Initiation - reaction initiated either thermally or photochemically, first reactive intermediates produced.

$\cdot Cl + O_3 \rightarrow \cdot ClO + O_2$

$\cdot ClO + O \rightarrow \cdot Cl + O_2$

Propagation - reaction of one chain carrier leads to formation of another.

$\cdot Cl + CH_4 \rightarrow \cdot CH_3 + HCl$

Termination - chain carriers are deactivated, often through radical-radical recombination, wall reactions or reaction to form inactive products.

May also have inhibition (retardation/de-propagation) steps, in which product molecules are destroyed.

Chain length $$n = \frac{\text{rate of propagation}}{\text{rate of initiation/termination}}$$

May be very long, up to 10^6 for the above reaction.

Examples of chain reactions

- Combustion of a fuel gas
- Development of rancidity in fats
- Polymerase chain reaction - “molecular photocopying” used to amplify DNA for analysis
- Polymerisation of ethene to polyethene
- Nuclear fission initiated by neutron bombardment

Types of chain reaction

Cyclic chain reactions - chain carriers are continuously regenerated until they are removed by a termination step (as in previous example)

Non-cyclic chain reactions - involve many reactive species and elementary steps. Can have extremely complicated kinetic mechanisms.

Linear chain reactions - each propagation step produces only one reactive intermediate.

Branched chain reactions - contains propagation steps that produce more than one reactive intermediate.

We will look at some examples of both linear and branched chain reactions

A linear chain reaction - the hydrogen-bromine (H_2 + Br_2) reaction

- 'Benchmark' system for illustrating chain reaction kinetics.

$$H_2 + Br_2 \rightarrow 2HBr$$

- First studied experimentally by Bodenstein around 100 years ago.

$$\frac{d[HBr]}{dt} = k\,[H_2][Br_2]^{1/2}$$

Early stages of reaction

$$\frac{d[HBr]}{dt} = \frac{k\,[H_2][Br_2]^{1/2}}{1 + k'\,[HBr]/[Br_2]}$$

Full rate law

- Any proposed mechanism must agree with both of these observations.

A linear chain reaction - the hydrogen-bromine (H_2 + Br_2) reaction

- The currently accepted thermal mechanism is

$Br_2 + M \xrightarrow{k_1} Br\cdot + Br\cdot + M$	Initiation
$Br\cdot + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H\cdot + HBr$	Propagation / Inhibition
$H\cdot + Br_2 \xrightarrow{k_3} Br\cdot + HBr$	Propagation
$Br\cdot + Br\cdot + M \xrightarrow{k_4} Br_2 + M$	Termination

- Initiation may also be photochemical: $Br_2 + h\nu \rightarrow Br + Br$
- Two chain carriers, H and Br
- Because the H-H bond is stronger than the H-Br bond, the reverse of the second step (an inhibition step) becomes possible when significant HBr has built up.

A linear chain reaction - the hydrogen-bromine ($H_2 + Br_2$) reaction

$$Br_2 + M \xrightarrow{k_1} Br\cdot + Br\cdot + M$$

$$Br\cdot + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H\cdot + HBr$$

$$H\cdot + Br_2 \xrightarrow{k_3} Br\cdot + HBr$$

$$Br\cdot + Br\cdot + M \xrightarrow{k_4} Br_2 + M$$

We can use the mechanism to derive a rate law.

- apply the SSA to H and Br.
- solve the SS equations to find [H] and [Br]
- substitute results into overall rate law.

① $$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_{-2}[H][Br] - k_3[H][Br_2]$$

② $$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2][M] - k_2[Br][H_2] + k_{-2}[H][HBr] + k_3[H][Br_2] - 2k_4[Br]^2[M]$$

Adding ① and ② gives

rate of initiation = rate of termination

③ $$0 = 2k_1[Br_2][M] - 2k_4[Br]^2[M] \Longrightarrow [Br] = \left(\frac{k_1[Br_2]}{k_4}\right)^{1/2}$$

This result also greatly simplifies ②, giving

$$[H] = \frac{k_2[Br][H_2]}{k_2[HBr] + k_3[Br_2]} = \frac{k_2[H_2]}{k_2[HBr] + k_3[Br_2]}\left(\frac{k_1[Br_2]}{k_4}\right)^{1/2}$$

A linear chain reaction - the hydrogen-bromine ($H_2 + Br_2$) reaction

$$Br_2 + M \xrightarrow{k_1} Br\cdot + Br\cdot + M$$

$$Br\cdot + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H\cdot + HBr$$

$$H\cdot + Br_2 \xrightarrow{k_3} Br\cdot + HBr$$

$$Br\cdot + Br\cdot + M \xrightarrow{k_4} Br_2 + M$$

$$[Br] = \left(\frac{k_1[Br_2]}{k_4}\right)^{1/2}$$

$$[H] = \frac{k_2[H_2]}{k_2[HBr] + k_3[Br_2]}\left(\frac{k_1[Br_2]}{k_4}\right)^{1/2}$$

- The overall rate is therefore

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[H][HBr] + k_3[H][Br_2]$$

$$= \frac{2k_2(k_1/k_4)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_{-2}/k_3)[HBr]/[Br_2]}$$

- In the early stages of the reaction, the HBr product concentration is much less than that of the reactant Br_2, and the second term in the denominator is negligible, giving

$$\frac{d[HBr]}{dt} = 2k_2(k_1/k_4)^{1/2}[Br_2]^{1/2}[H_2]$$

(early stages)

A linear chain reaction - the hydrogen-bromine ($H_2 + Br_2$) reaction

- Comparison between experimentally determined rate laws and those predicted by the mechanism using the steady-state approximation.

Early stages of reaction

$$\frac{d[HBr]}{dt} = k\,[H_2][Br_2]^{1/2}$$

Experiment

$$\frac{d[HBr]}{dt} = 2k_2(k_1/k_4)^{1/2}[Br_2]^{1/2}[H_2]$$

Predicted

Overall rate law

$$\frac{d[HBr]}{dt} = \frac{k\,[H_2][Br_2]^{1/2}}{1 + k'\,[HBr]/[Br_2]}$$

Experiment

$$\frac{d[HBr]}{dt} = \frac{2k_2(k_1/k_4)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_5/k_3)[HBr]/[Br_2]}$$

Predicted

- The predictions of the mechanism reproduce the experimental data.

What about the hydrogen-chlorine ($H_2 + Cl_2$) reaction?

- The mechanism is essentially identical to that for the $H_2 + Br_2$ reaction.

$Cl_2 + M \xrightarrow{k_1} Cl\cdot + Cl\cdot$ initiation

$Cl\cdot + H_2 \xrightarrow{k_2} H\cdot + HCl$ propagation

$H\cdot + Br_2 \xrightarrow{k_3} Cl\cdot + HCl$ propagation

$Cl\cdot + Cl\cdot + M \xrightarrow{k_4} Cl_2 + M$ termination

- Unlike $H_2 + Br_2$, both propagation steps are very efficient, and the inhibition step is very slow, giving a much higher overall reaction rate.

- Chain lengths up to 10^6 are possible, and coupled with the fact that the reaction is exothermic, this can lead to a thermal explosion (see later).

- We cannot carry out the same analysis on this reaction, because this reaction is a good example of a case in which the steady state approximation breaks down.

The $H_2 + Cl_2$ reaction - breakdown of the SSA

$Cl_2 + M \xrightarrow{k_1} Cl\cdot + Cl\cdot$ initiation

$Cl\cdot + H_2 \xrightarrow{k_2} H\cdot + HCl$ propagation

$H\cdot + Br_2 \xrightarrow{k_3} Cl\cdot + HCl$ propagation

$Cl\cdot + Cl\cdot + M \xrightarrow{k_4} Cl_2 + M$ termination

- Since both propagation steps are highly efficient, when $[H],[Cl] \ll [H_2],[Cl_2]$, a Cl atom is much more likely to collide with an H_2 molecule (propagation) than with a Cl atom (termination).

- This means that reaction may be quite advanced before the steady state condition is reached (that the rates of initiation and termination are equal).

- The situation is simplified by the fact that the reaction is extremely sensitive to inhibition by contaminants such as O_2.

$$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$$

$$Cl\cdot + O_2 + M \xrightarrow{k_6} \cdot ClO_2 + M$$

Dominant termination steps when $[O_2] > 1\%$

The H_2 + Cl_2 reaction - breakdown of the SSA

- The new mechanism is then

$Cl_2 + M \xrightarrow{k_1} Cl\cdot + Cl\cdot$ initiation

$Cl\cdot + H_2 \xrightarrow{k_2} H\cdot + HCl$ propagation

$H\cdot + Br_2 \xrightarrow{k_3} Cl\cdot + HCl$ propagation

$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$ termination

$Cl\cdot + O_2 + M \xrightarrow{k_6} \cdot ClO_2 + M$ termination

- Applying the SSA to [H] and [Cl] in the same way as we did for the H_2 + Br_2 reaction gives the following overall rate equation.

$$\frac{d[HCl]}{dt} = \frac{2k_a[H_2][Cl_2]^2}{[O_2]([H_2] + k_b[Cl_2])} \quad \text{with} \quad k_a = \frac{k_1 k_2}{k_5} \qquad k_b = \frac{k_3 k_6}{k_2 k_5}$$

Exercise: Prove this result!

How about the hydrogen-iodine ($H_2 + I_2$) reaction?

- We might expect a similar mechanism to the $H_2 + Br_2$ and $H_2 + Cl_2$ reactions.

- In fact, the mechanism is completely different, due to the fact that the reaction $I + H_2 \rightarrow H + HI$ (step 2) occurs far too slowly at normal temperatures for the $H_2 + Br_2$ mechanism to operate.

- Various mechanisms operate at different temperatures. e.g.

$$I_2 + M \rightleftharpoons I + I + M$$

$$I + I + H_2 \rightarrow 2HI$$

- Unlike the complicated rate laws for the Cl_2 and Br_2 reactions, the $H_2 + I_2$ reaction follows a simple second order rate law.

Comparison of the hydrogen + halogen reactions

$$Br_2 + M \xrightarrow{k_1} Br\cdot + Br\cdot + M$$

$$Br\cdot + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H\cdot + HBr$$

$$H\cdot + Br_2 \xrightarrow{k_3} Br\cdot + HBr$$

$$Br\cdot + Br\cdot + M \xrightarrow{k_4} Br_2 + M$$

- The key difference lies in the endothermicity of step 2 in the above mechanism for the three halogens

Cl	$\Delta H = 4.4$ kJ mol^{-1}	fast
Br	$\Delta H = 69.6$ kJ mol^{-1}	slow
I	$\Delta H = 137.7$ kJ mol^{-1}	does not occur

- The inhibition step, $H + HX \rightarrow X + H_2$, is thermodynamically favourable for both Cl and Br.

- In the Cl_2 reaction this step is unimportant due to the very low steady-state concentration of H atoms.

- In the Br_2 reaction, the inhibition step has a considerable effect on the overall reaction kinetics.

Explosions

- Explosions occur when a reaction rate accelerates out of control.
- The resulting series of events often occur within a tiny fraction of a second:
  - gaseous products are formed in larger and larger amounts, and more and more heat is generated.
  - Rapid liberation of heat causes the gases to expand, generating high pressures.
  - The sudden formation of a huge volume of expanded gas constitutes the explosion.
  - The pressure wave travels at very high speeds. The “bang” associated with an explosion is the result of a supersonic shock wave.

Explosion mechanisms

Reaction rates depend on both the magnitude of the rate constant and on the amounts of reactants present, leading to two possible explosion mechanisms.

Thermal explosions

- Occur when the heat generated by a reaction cannot be dissipated sufficiently rapidly.
- The temperature of the reaction mixture rises, which increases the rate constant and therefore the reaction rate, leading to a further increase in temperature, and so on.
  e.g. detonation of TNT is the result of an extremely fast chemical decomposition that generates huge quantities of gas.

rather misleading!

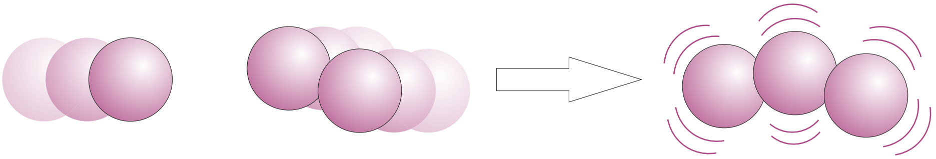
Chain branching explosions ("isothermal explosions")

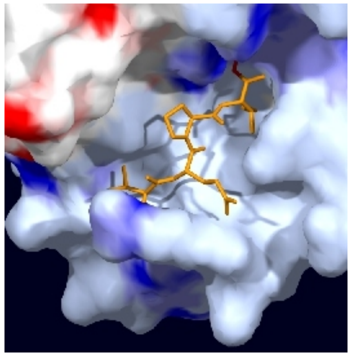
- One or more steps in the reaction mechanism produce two or more chain carriers from one chain carrier, leading to a rapid increase in the number of chain carriers, and therefore the overall reaction rate.

Both mechanisms often operate simultaneously, since any acceleration in the rate of an exothermic reaction will eventually lead to an increase in T.

Summary of last lecture

- We looked at the kinetics of third order reactions, enzyme reactions and chain reactions.





- We started to look at explosions:
  - An explosion occurs when a reaction rate accelerates out of control and generates a high pressure of gaseous products in a very short space of time.

  - Explosions can be caused by a rapid increase in the rate constant (a thermal explosion) or the amounts of reactants (chain branching or isothermal explosion).
  - We will use the reaction of H_2 and O_2 to form H_2O as an example.

The hydrogen + oxygen reaction, $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

- An example of a reaction in which both the thermal and chain branching explosion mechanisms are important.

- The reaction mechanism is extremely complex and still not completely understood, but is known to be a branched chain reaction involving chain carriers such as H, O and OH.

- A simplified version of the mechanism is:

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} \text{H-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} \text{O-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} \text{OH-wall}$	termination

The hydrogen + oxygen reaction

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} \text{H-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} \text{O-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} \text{OH-wall}$	termination

- The net result of the two branching steps is $H\cdot + O_2 + H_2 \rightarrow H\cdot + \cdot OH + \cdot OH$. giving an overall branching ratio of 3.

- Steps 1, 2, and 3 are endothermic, and therefore slow at room temperature.

- The efficiency of the branching steps increases with increasing temperature.

- The result is that the reaction shows a complicated dependence on temperature and pressure.

The hydrogen + oxygen reaction - explosion limits

$\mathrm{H_2 + wall \xrightarrow{k_1} H\cdot + H\cdot + wall}$ initiation

$\mathrm{H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot}$ branching

$\mathrm{\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot}$ branching

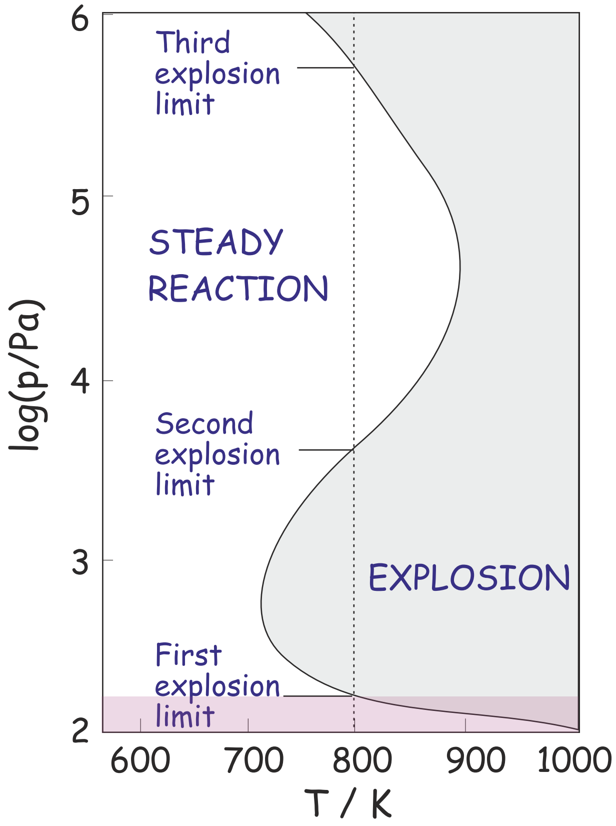
$\mathrm{\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O}$ propagation

$\mathrm{H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M}$ termination

$\mathrm{H\cdot + wall \xrightarrow{k_6} H\text{-}wall}$ termination

$\mathrm{\cdot O\cdot + wall \xrightarrow{k_7} O\text{-}wall}$ termination

$\mathrm{\cdot OH + wall \xrightarrow{k_8} OH\text{-}wall}$ termination

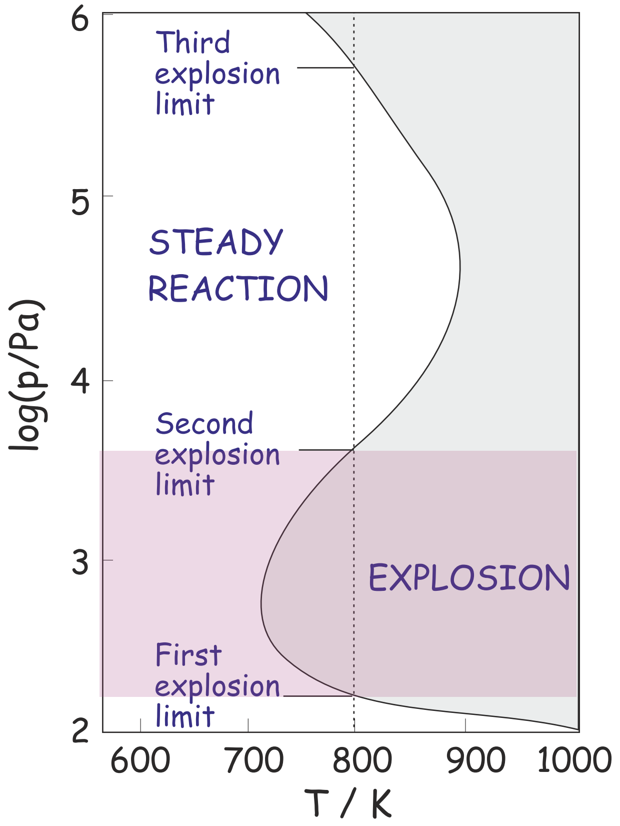


- At very low pressures, the mean free path in the gas is large, and collisions with walls are more likely than with other gas molecules.

- Overall, $\nu_5 + \nu_6 + \nu_7 + \nu_8 = \nu_1 + \nu_2 + \nu_3$, (termination balances initiation), and steady reaction occurs.

The hydrogen + oxygen reaction - explosion limits

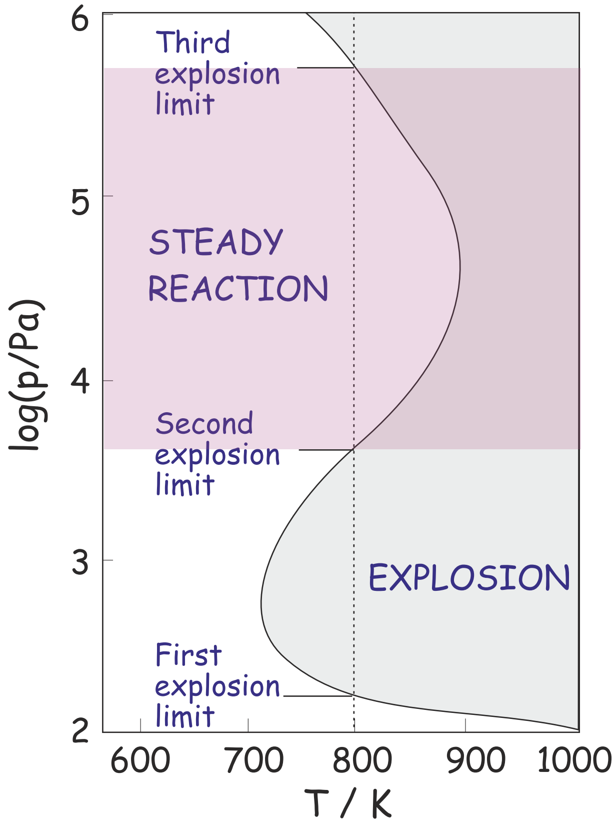
$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination



- At higher pressures, chain carriers react before reaching the walls.
- For gas phase reactions, rate α p^2, and for wall reactions rate α p, so the gas phase branching reactions soon become too fast for wall termination to control.
- We now have $\nu^1 + \nu^2 + \nu^3 > \nu^5 + \nu^6 + \nu^7 + \nu^8$, and the mixture becomes explosive (the first explosion limit)

The hydrogen + oxygen reaction - explosion limits

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination



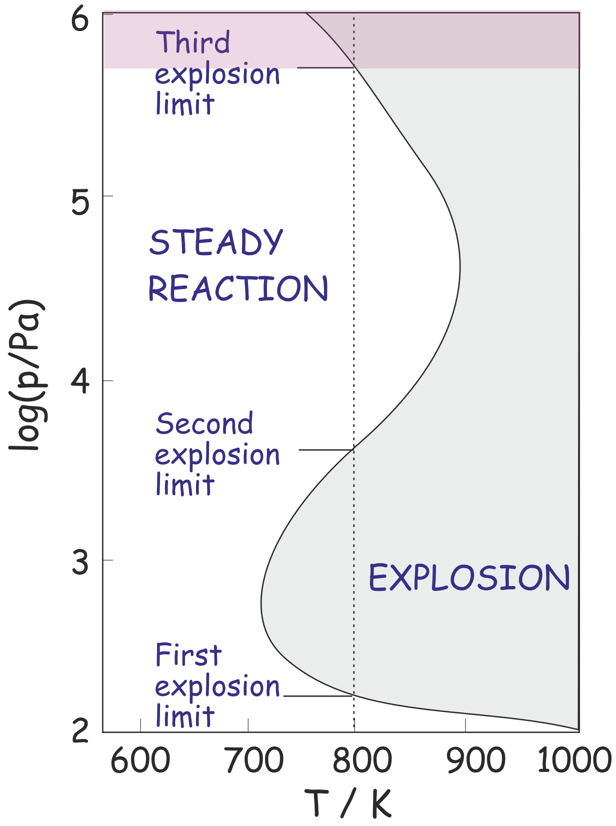
- At still higher pressures, three body collisions start to become important.

- Termination step 5 can now match steps 1-3 in efficiency, and we again have $\nu^5 + \nu^6 + \nu^7 + \nu^8 = \nu^1 + \nu^2 + \nu^3$ and steady reaction.

- This is the second explosion limit.

The hydrogen + oxygen reaction - explosion limits

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination

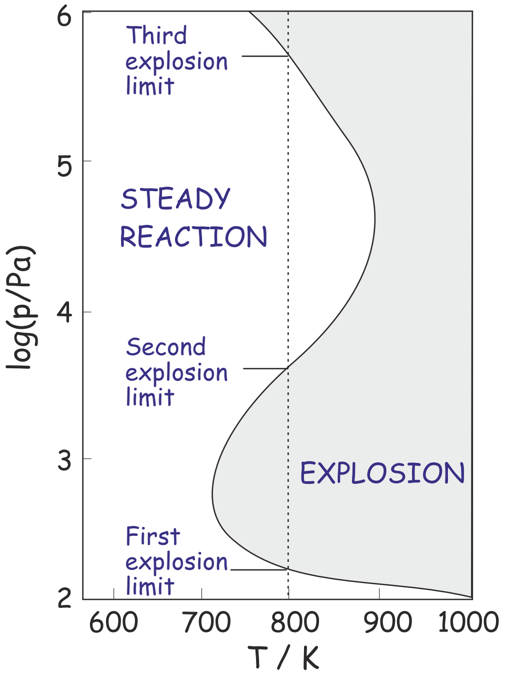


- If the pressure is increased even further, the rate increases so much and so much heat is generated that a thermal explosion results.

- This is the third explosion limit.

The hydrogen + oxygen reaction - factors affecting the limits

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination

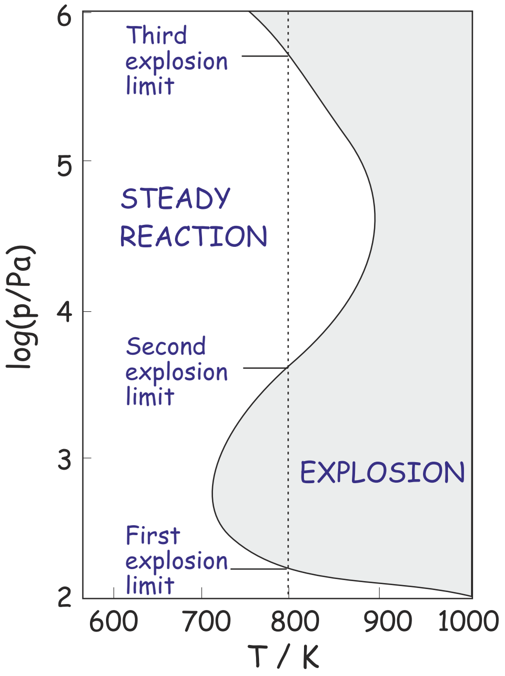


Temperature

- Increasing T increases the efficiency of steps 1-4, which are either endothermic or possess an activation barrier.
- The termination steps are less sensitive to temperature, and may even be slowed down due to their exothermicity.
- The first explosion limit is lowered, as 2 and 3 outpace 6-8 more easily.
- The second limit is raised, since a higher pressure is needed for 5 (termolecular) to become important.
- The third limit is lowered, since more heat is produced at higher temperature and it is also harder to dissipate from the system.

The hydrogen + oxygen reaction - factors affecting the limits

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination

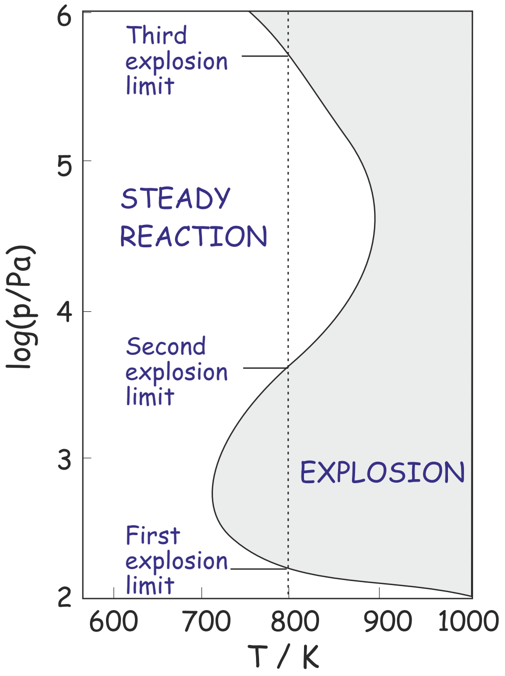


Shape and size of reaction vessel (surface to volume ratio)

- Increasing the surface to volume ratio favours wall processes (1, 6, 7, 8) over gas phase processes.
- High efficiency of branching steps makes 1 unimportant in determining overall rate, so the increased efficiency of the termination steps raises the pressure at which the first explosion limit occurs.
- The second explosion limit has no dependence on the walls and is unchanged.
- The third limit is raised because a larger surface area makes it easier to lose heat through collisions with the walls.

The hydrogen + oxygen reaction - factors affecting the limits

$H_2 + \text{wall} \xrightarrow{k_1} H\cdot + H\cdot + \text{wall}$	initiation
$H\cdot + O_2 \xrightarrow{k_2} \cdot OH + \cdot O\cdot$	branching
$\cdot O\cdot + H_2 \xrightarrow{k_3} \cdot OH + H\cdot$	branching
$\cdot OH + H_2 \xrightarrow{k_4} H\cdot + H_2O$	propagation
$H\cdot + O_2 + M \xrightarrow{k_5} \cdot HO_2 + M$	termination
$H\cdot + \text{wall} \xrightarrow{k_6} H\text{-wall}$	termination
$\cdot O\cdot + \text{wall} \xrightarrow{k_7} O\text{-wall}$	termination
$\cdot OH + \text{wall} \xrightarrow{k_8} OH\text{-wall}$	termination



Overall pressure

- Adding an inert gas decreases the mean free path of the gas, and disfavours collisions with the walls.

- The first explosion limit is lowered since 6,7,8 become less efficient.

- The second limit is also lowered since the inert gas can act as the third body, increasing the rate of 5.

- The third limit is lowered due to the reduced heat transfer from the gas to the vessel walls.

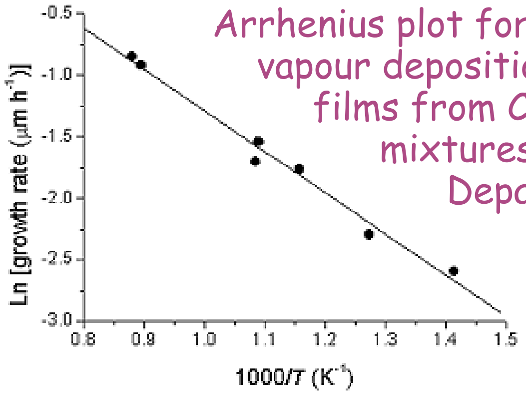
Temperature dependence of chemical reactions

- It is found experimentally that the rate constants for many chemical reactions follow the Arrhenius equation.

$$k = A\exp(-E_a/RT) \qquad \ln k = \ln A - \frac{E_a}{RT}$$

- The Arrhenius parameters, A and E_a, may be found from an Arrhenius plot of lnk vs 1/T.

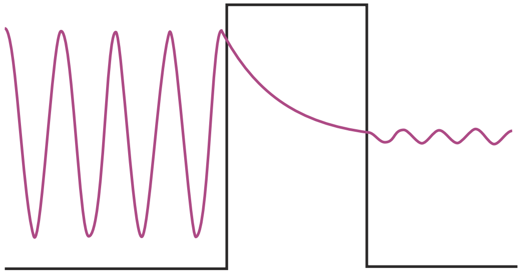
- The Arrhenius equation works reasonably well over at least a limited range of temperatures, but there are often deviations.



Arrhenius plot for the chemical vapour deposition of diamond films from CO_2/ CH_4 gas mixtures (Bristol Department of Chemistry)

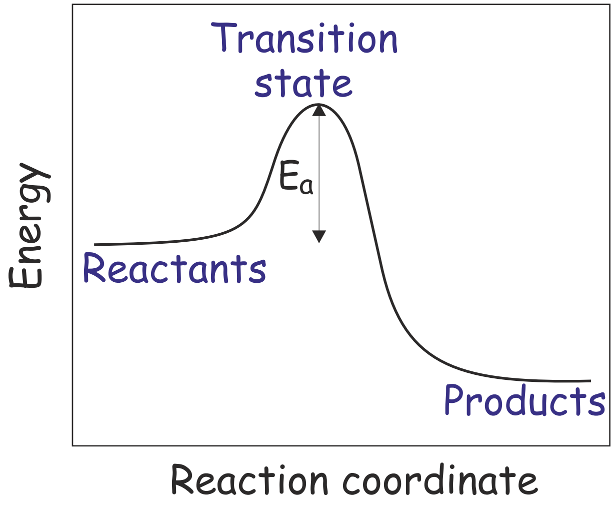
- Deviations are often due to the fact that the pre-exponential factor is in fact temperature dependent (see simple collision theory and statistical mechanics).

- Deviations at low temperatures may be due to quantum-mechanical tunnelling through the activation barrier, particularly for electron or proton transfer reactions.



Inside barrier $\psi(x) = Ae^{-\alpha x}$ with $\alpha = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$

Activation energies



$$k = A\exp(-E_a/RT)$$

- For an elementary reaction, E_a and A have definite physical meanings (A = collision rate, E_a = barrier height).

- When the Arrhenius equation is applied to the overall rate of a multi-step reaction, E_a simply becomes an experimental parameter describing the temperature dependence of the overall rate.

$$E_a = RT^2\frac{d\ln k}{dT}$$

- E_a may be temperature dependent, and may be positive or negative.

- Equivalent to the Arrhenius equation when E_a is independent of temperature.

- We can use this definition to determine E_a at a given temperature from a plot of lnk vs T, even if the plot is not linear.

Activation energies - interpretations

Several observations follow from this definition of the activation energy.

$$E_a = RT^2 \frac{d\ln k}{dT}$$

1. The higher the activation energy, the stronger the temperature dependence of the rate constant.

2. A reaction with no temperature dependence has an activation energy of zero (common in ion-molecule reactions and radical-radical recombinations)

3. A negative activation energy implies that the rate decreases as the temperature increases, and always indicates a complex mechanism.

e.g.

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NO)_2$$

$$(NO)_2 + O_2 \xrightarrow{k_2} 2NO_2$$

Explain in terms of lifetime of $(NO)_2$ complex (or Le Chatelier's principle)

Overall activation energies for complex reactions

- The Arrhenius equation may often be used to estimate the overall activation energy when the activation energies for individual steps are known.

$$\mathrm{NO + NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{(NO)_2}$$

$$\mathrm{(NO)_2 + O_2} \xrightarrow{k_2} \mathrm{2NO_2}$$

$$\nu = \frac{k_1k_2}{k_{-1}}[\mathrm{NO}]^2[\mathrm{O_2}] = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

overall third order rate constant

- The temperature dependence of the overall rate constant is

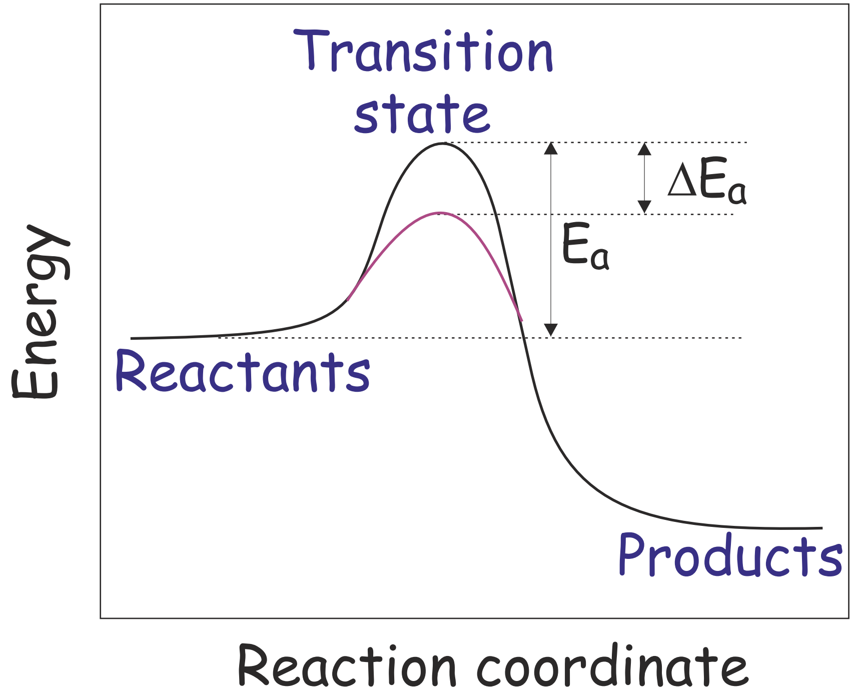
$$k = \frac{k_1k_2}{k_{-1}} = \frac{A_1\exp\left(\frac{-E_a^{(1)}}{RT}\right)A_2\exp\left(\frac{-E_a^{(2)}}{RT}\right)}{A_{-1}\exp\left(\frac{-E_a^{(-1)}}{RT}\right)} = \frac{A_1A_2}{A_{-1}}\exp\left(\frac{-E_a^{(1)}-E_a^{(2)}+E_a^{(-1)}}{RT}\right)$$

- We can therefore identify A and E_a for the overall reaction.

$$A = \frac{A_1A_2}{A_{-1}} \qquad E_a = E_a^{(1)} + E_a^{(2)} - E_a^{(-1)}$$

Catalysis

- A catalyst works by lowering the activation energy for a reaction. We can see from the Arrhenius equation that this will have the effect of increasing the rate constant.



$$k = A\exp[-E_a/RT]$$

$$k_{cat} = A\exp[-(E_a-\Delta E_a)/RT)]$$

$$= A\exp[\Delta E_a/RT]\exp[-E_a/RT]$$

$$= \underbrace{\exp[\Delta E_a/RT]}_{\text{The rate constant increases by this factor}}\,k$$

Simple collision theory

- One of the most basic attempts to develop a theory capable of predicting the rate for an elementary bimolecular reaction.

$$A + B \rightarrow P$$

What factors do we expect the reaction rate to depend upon?

1. The rate must depend on the frequency of collisions between the reactants.

2. Not every collision leads to reaction, due to the reactants not having sufficient energy to surmount the activation barrier. This energetic requirement must be taken into account.

3. Even when the energy requirement is met, reaction still may not occur, due to incorrect molecular orientations (e.g. S_N2 reactions) or the energy being in the wrong degree of freedom (e.g. may need vibration in a bond coupled to the reaction coordinate).

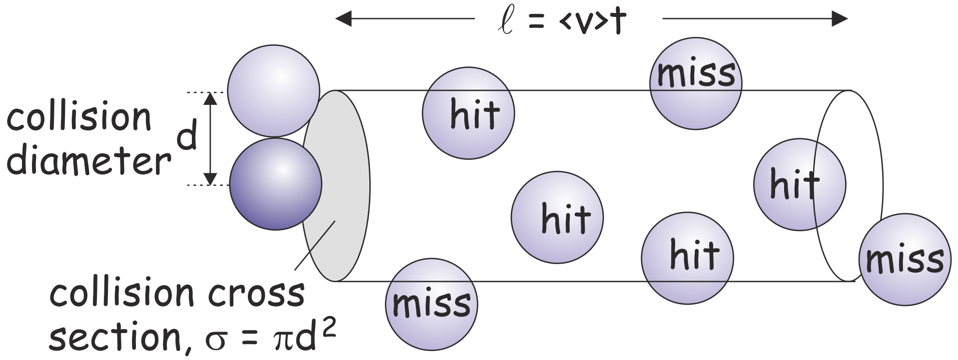
i.e. our equation for the rate will take the form

rate = (encounter rate) (energy requirement) (steric requirement)

Collisions with other molecules - the collision cross section

- We need to introduce the concept of a collision cross section before we can treat molecular collisions.

- The dark blue particle will only collide with other particles whose centres lie within the cross-sectional area $\sigma = \pi d^2$.



- If the blue particle is travelling with average velocity <v>, then in a time t it will cover a distance <v>t and sample a volume σ<v>t.

- The number of particles within this volume (and therefore the number of collisions the blue particle undergoes) is simply this 'collision volume' multiplied by the particle number density $n = N/V = p/k_BT$. Per second, the number of collisions is:

$$z = \underbrace{\sigma \langle v_{rel} \rangle}_{\text{collision volume per unit time}} \underbrace{\frac{N}{V}}_{\text{number density}} = \sigma \langle v_{rel} \rangle \frac{p}{k_B T}$$

Note that we use $\langle v_{rel} \rangle$ to account for the fact that the other particles are also moving.

Collision cross sections and rate constants

- A single particle colliding with other particles is a first order rate process.
- Compare our expression for the collision rate with a first order rate law.

$$z = \sigma \langle v_{rel} \rangle \frac{N}{V} \qquad\qquad \text{rate} = k[A]$$

- The number density is the gas-phase equivalent of a concentration, so the quantity $\sigma\langle v_{rel}\rangle$ is in fact a "molecular scale" rate constant.
- Usually we want to know the total collision frequency (or collision density), i.e. the total number of collisions occurring per unit volume per unit time. This is a second order rate process, with rate $k(N/V)^2$.

$$Z_{XX} = \frac{1}{2} \sigma \langle v_{rel} \rangle \left(\frac{N_X}{V}\right)^2 \qquad \text{or} \qquad Z_{XY} = \sigma \left(\frac{8k_BT}{\pi\bar{\mu}}\right)^{1/2} n_X n_Y$$

Avoids double counting of collisions (X colliding with X' is the same collision as X' colliding with X)

Note: the collision diameter in $\sigma = \pi d^2$ is now $d = (d_X+d_Y)/2$

<u>Example</u>: In N_2 gas under standard conditions, $Z_{XX} = 5 \times 10^{34}\ s^{-1}\ m^{-3}$.

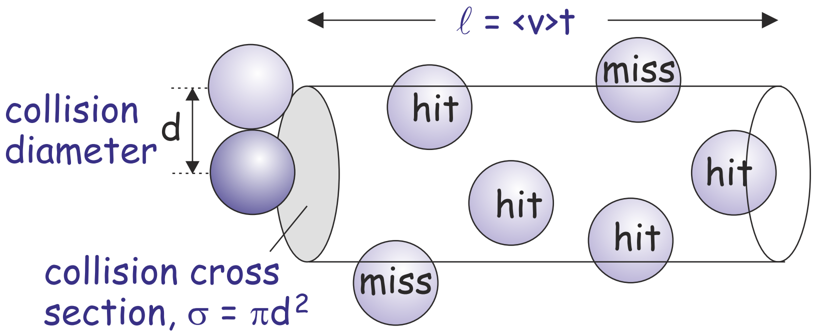
Simple collision theory

rate = (encounter rate) (energy requirement) (steric requirement)

1. Encounter rate

- We have just showed that the rate of collisions between molecules A and B present at number densities n_A and n_B is

$$Z_{AB} = \sigma_C \left(\frac{8kT}{\pi\mu}\right)^{1/2} n_A n_B$$



2. Energy requirement

- For a Maxwell-Boltzmann distribution of molecular speeds, the fraction of collisions for which the energy is high enough to overcome the activation barrier is

$$\exp(-E_a/RT)$$

Simple collision theory

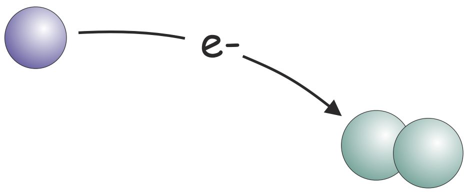
rate = (encounter rate) (energy requirement) (steric requirement)

3. Steric requirement

- So far, we would predict that the rate is given by:

$$\nu = \sigma_C \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(\frac{-E_a}{RT}\right) n_A n_B$$

- However, rates are often found to be up to an order of magnitude smaller than predicted by this expression.
- Suggests that factors such as relative orientation of the reactants must be important.
- Accounted for by introducing a 'steric factor', P, into our expression, or alternatively, replacing the collision cross section σ_C with a reaction cross section σ_R (with $\sigma_R = P\,\sigma_C$)
- Note that P may also be greater than one e.g. 'harpoon' reaction between Rb and Cl_2.



Simple collision theory

rate = (encounter rate) (energy requirement) (steric requirement)

- Our final expression for the rate is therefore

$$\nu = \underbrace{P\,\sigma_C\left(\frac{8kT}{\pi\mu}\right)^{1/2}\exp\left(\frac{-E_a}{RT}\right)}_{\text{second order rate constant}} n_A n_B$$

- Simple collision theory is a good first attempt at rationalising the Arrhenius temperature dependence of many rate constants, but there are a number of shortcomings.

1. Unless the collision is head on, not all of the kinetic energy of the reactants is available for the reaction (conservation of momentum means that only the kinetic energy of <u>relative</u> motion contributes).

2. Energy stored in internal degrees of freedom (rotation, vibration) of the reactants has been ignored. This is treated properly in transition state theory.

THE END IS NEAR

Course summary

1. Reaction potential energy surfaces and kinetics at the molecular level.

2. Rates of reaction and rate laws.

3. Experimental techniques for measuring reaction rates.

4. Determining the rate law from experimental data.

5. Multi-step ('complex') reactions of various types:
    - unimolecular reactions;
    - third order reactions;
    - enzyme reactions;
    - chain reactions and explosions.

6. Temperature dependence of reaction rates.

7. Simple collision theory.