Lecture 10-11

Chemical Kinetics: Integrated rate equations

Chemical Kinetics: time course of chemical transformation

Thermodynamics tells us whether a chemical reaction is possible or not. Chemical kinetics tells us how fast a particular chemical reaction will proceed. Chemical kinetics deals with the rate of change of chemical transformations i.e. how quickly reactant molecules transform to products.
Chemically relevant questions.

- What can we say about chemical reactions?
  - Reactants mix and products form.
  - A balanced equation is essential quantitative tool for calculating product yields from reaction amounts.
- What about the dynamics of chemical reactions?
  - Useful questions that require answers include:
    - Will the reaction proceed by itself and release energy, or will it require energy to proceed?
      - Thermodynamics (free energy) and thermochemistry.
    - What will the reactant and product concentrations be when the reaction is complete?
      - Thermodynamics and chemical equilibrium.
    - How fast is the chemical reaction proceeding at a given moment?
      - Chemical kinetics.
- An essential concept in chemical kinetics is that of chemical reaction rate. This is defined in terms of the change in species concentration (amount per unit volume, i.e. mol/L) with respect to time (s).

**Timescales in Chemical Kinetics**

![Diagram showing timescales from milliseconds to femtoseconds](image)

Experimental timescales range from minutes (typical JF/SF kinetics experiments) down to femtoseconds. 1 femtosecond (fs) = \(10^{-15}\) s
Sometimes chemical reactions proceed too quickly!

Why is chemical kinetics useful?  
The ozone layer hole and atmospheric kinetics

The increasing size of the Antarctic ozone hole.
Basic ideas in reaction kinetics.

- Chemical reaction kinetics deals with the rate of velocity of chemical reactions.

- We wish to quantify
  - The velocity at which reactants are transformed to products
  - The detailed molecular pathway by which a reaction proceeds (the reaction mechanism).

- These objectives are accomplished using experimental measurements.

- We are also interested in developing theoretical models by which the underlying basis of chemical reactions can be understood at a microscopic molecular level.

- Chemical reactions are said to be activated processes: energy (usually thermal (heat) energy) must be introduced into the system so that chemical transformation can occur. Hence chemical reactions occur more rapidly when the temperature of the system is increased.

- In simple terms an activation energy barrier must be overcome before reactants can be transformed into products.

Reaction rate: definition

- What do we mean by the term reaction rate?
  - The term rate implies that something changes with respect to something else.

- How may reaction rates be determined?
  - The reaction rate is quantified in terms of the change in concentration of a reactant or product species with respect to time.
  - This requires an experimental measurement of the manner in which the concentration changes with time of reaction. We can monitor either the concentration change directly, or monitor changes in some physical quantity which is directly proportional to the concentration.

- The reactant concentration decreases with increasing time, and the product concentration increases with increasing time.

- The rate of a chemical reaction depends on the concentration of each of the participating reactant species.

- The manner in which the rate changes in magnitude with changes in the magnitude of each of the participating reactants is termed the reaction order.
Reaction rate can be quantified by monitoring changes in either reactant concentration or product concentration as a function of time.

Initial rate determined by evaluating tangent to concentration versus time curve at a given time $t_0$.

Working out a rate equation.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_3(g)$$

Initial rate is proportional to initial concentration of reactant.

$$k = \text{rate constant}$$
Reaction rate varies with extent of reaction.
Rate constant \( k \) stays constant over duration of reaction.
Value depends on temperature of reaction medium only.
Rate constant \( k \) is a good indicator of reaction velocity.

For a first order reaction the following relationship between rate and concentration is valid for any time \( t \):

\[
\begin{align*}
R &= \frac{d[A]}{dt} = kc \\
R &\propto [A] = c \\
\end{align*}
\]

**First order kinetics**

- The rate equation must be integrated to obtain an expression for the reactant concentration as a function of time.
- To do this we need an initial condition which tells us the reactant concentration at zero time.

\[
\frac{dc}{dt} = kc \\

t = 0 \quad c = c_0
\]
Rate equation

- The reaction rate (reaction velocity) \( R \) is quantified in terms of changes in concentration \( [J] \) of reactant or product species \( J \) with respect to changes in time.
- The magnitude of the reaction rate changed as the reaction proceeds.
- Rate of reaction is often found to be proportional to the molar concentration of the reactants raised to a simple power (which need not be integral). This relationship is called the rate equation.
- The manner in which the reaction rate changes in magnitude with changes in the magnitude of the concentration of each participating reactant species is called the reaction order.
- The components of the rate equation:
  - rate
  - rate constant
  - reactant reaction order
- must always be determined experimentally.
- An experimental approach to finding the components is:
  - Use concentration vs time measurements to find the initial rate.
  - Use initial rates from several experiments to determine the rate orders for each participating reactant species.
  - Use this data to calculate the rate constant.

\[
\text{Rate} = \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt}
\]

\[
\text{Rate} = k[A]^a[B]^b
\]

\( k \) = rate constant
\( a, b \) = reaction orders

Reaction Order:
The reaction order is a measure of the sensitivity of the reaction rate to changes in the concentration of the reactants.

Note: Units of rate: \( - \) concentration/time

\[
R_J = \lim_{\Delta t \to 0} \frac{\Delta [J]}{\Delta t} = \frac{1}{v_J} \frac{d[J]}{dt}
\]

Kinetics of oxidation of iodide ion by peroxydisulfate ion.

- In this lab experiment you are asked to determine the rate equation, reaction order and rate constant for the electron transfer or redox reaction.
- Reaction is thermodynamically favoured (\( \Delta G^0 = -285 \text{ kJ mol}^{-1} \)), but occurs slowly, so that the kinetics can be readily measured.
- We measure the initial rate. Here we make a rate measurement under conditions where the reactant concentrations have hardly changed from their initial values.
- We use a very sensitive method to measure the time \( \Delta t \) taken for a fixed quantity of iodine \( (I_2) \) to be generated, and hence by stoichiometry, for a fixed quantity \( (A[S_2O_8^{2-}]) \) of peroxydisulfate ion to be lost. Hence the rate \( R \) can be calculated.
- This is done by adding to the reaction mixture a fixed quantity of thiosulfate which reacts very quickly with any iodine molecules generated. We also add some starch indicator to the reaction mixture.
- When all thiosulfate ions are consumed the starch will react quickly with further iodine molecules generated in the oxidation reaction and the solution will become blue.
- The time \( \Delta t \) taken between the mixing of the reactants and the appearance of the blue colour corresponds to the time taken for all the known amount of added thiosulfate ion to be consumed.
- By stoichiometry we can then calculate the corresponding quantity of peroxydisulfate consumed during this period.
- Reaction orders \( x \) and \( y \) obtained by measuring initial reaction rate for various initial concentrations of iodide and peroxydisulfate ions. We show that \( x = 1 \) and \( y = 1 \).
Determination of reaction order via the initial rate method.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$[O_2]_0$</th>
<th>$[NO]_0$</th>
<th>Initial rate Mol L$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1x10$^{-2}$</td>
<td>1.3x10$^{-2}$</td>
<td>3.21x10$^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>2.2x10$^{-2}$</td>
<td>1.3x10$^{-2}$</td>
<td>6.40x10$^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>1.1x10$^{-2}$</td>
<td>2.6x10$^{-2}$</td>
<td>12.80x10$^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>3.3x10$^{-2}$</td>
<td>1.3x10$^{-2}$</td>
<td>9.60x10$^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>1.1x10$^{-2}$</td>
<td>3.9x10$^{-2}$</td>
<td>28.80x10$^{-3}$</td>
</tr>
</tbody>
</table>

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$

$R = k[O_2]^\alpha[NO]^\beta$

We want to evaluate the reaction orders $\alpha$ and $\beta$ from the initial rate data.

Experiment 1 & 2.

$[NO]_1 = [NO]_2$

$\frac{R_2}{R_1} = \frac{k[O_2]^\alpha[NO]^\beta}{k[O_2]^\alpha[NO]^\beta} = \frac{[O_2]^\alpha}{[O_2]^\alpha} = \frac{[O_2]^\alpha}{[O_2]^\alpha}$

$6.4 \times 10^{-3} = \left( \frac{2.2 \times 10^{-2}}{1.1 \times 10^{-2}} \right)^\alpha$

$1.99 = 2^\alpha$

$\log(1.99) = \alpha \log(2)$

$\alpha = \frac{\log(1.99)}{\log(2)} = \frac{\log 2}{\log 2} = 1$

Hence reaction is first order wrt $O_2$.
When $[O_2]$ doubles, the rate doubles.

Experiment 3 & 1.

$[O_2]_3 = [O_2]_1$

$\frac{R_4}{R_1} = \frac{k[O_2]^\alpha[NO]^\beta}{k[O_2]^\alpha[NO]^\beta} = \frac{[NO]^\beta}{[NO]^\beta}$

$12.8 \times 10^{-3} = \left( \frac{2.60 \times 10^{-2}}{1.30 \times 10^{-2}} \right)^\beta$

$3.99 = 2^\beta$

$\log 4 = \beta \log 2$

$\beta = \frac{\log 4}{\log 2} = 2$

Hence reaction is second order wrt $NO$.
When $[NO]$ doubles the rate quadruples.

We conclude that the rate law is given by the expression outlined across.

$R = k[O_2][NO]^2$
Reaction order determination.

Vary [A], keeping [B] constant and measure rate R.
Vary [B], keeping [A] constant and measure rate R.

Rate equation cannot in general be inferred from the stoichiometric equation for the reaction.

Rate orders obtained from the slope of log/log plots.

The bottom line.
A rationale and procedure for the study of chemical kinetics.

- Get the concentration versus time data.
- Figure out what mathematical expression the data fit.
- Deduce the rate law.
- Evaluate the rate constant.
- Work out a mechanism consistent with the rate law.
- Do something useful: speed up, slow down or control the reaction.

Chemistry, Chapter 8, pp. 339-398.
Atkins de Paula, 5th edition, Chapter 10, pp. 219-240.
Quantitative Chemical Kinetics

- The kinetics of a chemical reaction are quantified by determining the rate constant $k$.
- This is usually done by measuring changes in the reactant or product concentration (or some physical quantity such as optical absorbance or conductivity proportional to concentration) as a function of time.
- The rate equation is formulated from the experimental data.
- If the rate equation (which relates reaction rate to reactant concentration) can be cast into one of a number of standard types, then it can be analytically integrated using suitable methods to obtain a mathematical expression for the concentration as a function of time.
- This concentration/time relationship can then be manipulated to generate a linear equation which can be graphed. The rate constant is then obtained from the graph.

- We shall look at a number of simple examples of chemical reactions which may be subjected to quantitative mathematical analysis. There are many more of course. As the reaction gets more complex the degree of complexity involved in integrating the rate equation increases.
- It is important to note that the rate constant must be measured at a constant temperature, since it will only be constant under such conditions.
- Also the time scale involved in the chemical reaction (can vary from 10^{-12} s to minutes) will determine the type and sophistication of the experimental technique used to measure the rate constant. The shorter the timescale probed, the more sophisticated (and expensive) is the experimental methodology employed.

Zero Order Kinetics:
Integrated rate equation.

- Applicable to chemical reactions on surfaces.
- Reaction proceeds at the same rate regardless of reactant concentration.
- Hence rate is independent of concentration.

\[ c = c_0 \quad t = 0 \]

\[
R = -\frac{dc}{dt} = k \\
c(t) = -kt + c_0
\]
Zero order kinetics: half life.

- **Half life** $\tau_{1/2}$:
  - Time taken for concentration of reactant to fall to 50% of its initial value.
  - Half life will always be inversely proportional to the rate constant since a large rate constant will always imply a short half life and vice versa.
  - The half life is directly proportional to the initial reactant concentration for a reaction exhibiting zero order kinetics.

\[
t = \tau_{1/2} \quad \text{when} \quad c(t) = \frac{c_0}{2}
\]

\[
c(t) = -kt + c_0
\]

\[
\frac{c_0}{2} = -k\tau_{1/2} + c_0
\]

\[
\tau_{1/2} = \frac{c_0}{2k}
\]

First order kinetics:
Integrated rate equation

\[A \xrightarrow{k} \text{Products}\]

Chemistry 3 Box 8.1
p. 350 Derivation.

\[-\frac{dc}{dt} = kc\]

Initial condition

\[t = 0 \quad c = c_0\]

Solve differential equation
Separation of variables

\[c(t) = c_0e^{-kt} = c_0 \exp[-kt]\]

\[\ln c(t) = -kt + \ln c_0\]

$k = \text{first order rate constant, units: s}^{-1}$

A plot of $\ln c(t)$ as function of time $t$ is diagnostic of 1st order kinetics.
First order kinetics: half life

\[ t = \frac{1}{2} \tau \quad c = \frac{c_0}{2} \]

In each successive period of duration \( \tau/2 \), the concentration of a reactant in a first order reaction decays to half its value at the start of that period. After \( n \) such periods, the concentration is \((1/2)^n\) of its initial value.

[Image of concentration vs. time graph]

Second Order Kinetics: Equal reactant concentrations.

Rate equation

\[ \frac{dc}{dt} = 2kc^2 \quad t = 0 \quad c = c_0 \]

separate variables

\[ \frac{1}{c} = 2kt + \frac{1}{c_0} \]

integrate

\[ c(t) = \frac{c_0}{1 + 2kc_0 t} \]

Half life

\[ \tau_{1/2} = \frac{1}{2kc_0} \]

rate varies as square of reactant concentration

Half life inversely proportional to initial reactant concentration.

[Image of concentration vs. time graph]
Table 8.2 A summary of equations for elementary reactions

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Order of reaction</th>
<th>Differential rate equation</th>
<th>Integrated rate equation</th>
<th>Half life, $t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $\rightarrow$ products</td>
<td>First order</td>
<td>$-\frac{d[A]}{dt} = k[A]$</td>
<td>$\ln[A]_0 = \ln[A]_t - kt$</td>
<td>$\frac{1}{k}$</td>
</tr>
<tr>
<td>A + A $\rightarrow$ products</td>
<td>Second order</td>
<td>$-\frac{d[A]}{dt} = 2k[A]^2$</td>
<td>$\frac{1}{[A]_0} = \frac{1}{[A]_t} + 2kt$</td>
<td>$\frac{1}{2k[A]_0}$</td>
</tr>
<tr>
<td>A + B $\rightarrow$ products</td>
<td>Pseudo-first order where [A] = [B]</td>
<td>$-\frac{d[A]}{dt} = k'[A]$</td>
<td>$\ln[A]_t = \ln[A]_0 - k't$</td>
<td>$\frac{1}{k'[A]_0}$</td>
</tr>
</tbody>
</table>

Table 8.3 Using integrated rate equations to study complex reactions

<table>
<thead>
<tr>
<th>Order</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate equation</td>
<td>Rate $= k'$</td>
<td>Rate $= k[A]$</td>
<td>Rate $= k[A]^2$</td>
</tr>
<tr>
<td>Integrated rate equation</td>
<td>$[A]_t = [A]_0 - k't$</td>
<td>$\ln[A]_t = \ln[A]_0 - k't$</td>
<td>$\frac{1}{[A]_0} = \frac{1}{[A]_t} + 2kt$</td>
</tr>
<tr>
<td>Plot of $[A]$ vs $t$</td>
<td>Straight</td>
<td>Curve</td>
<td>Curve</td>
</tr>
<tr>
<td>Plot of $\ln[A]$ vs $t$</td>
<td>Curve</td>
<td>Curve</td>
<td>Straight line</td>
</tr>
<tr>
<td>Plot of $\frac{1}{[A]}$ vs $t$</td>
<td>Curve</td>
<td>Curve</td>
<td>Straight line</td>
</tr>
<tr>
<td>Half life, $t_{1/2}$</td>
<td>Not constant</td>
<td>Constant</td>
<td>Not constant</td>
</tr>
</tbody>
</table>

* The multiplication factor before $k'$ depends on the stoichiometry of the reaction.
Lecture 12

Chemical Kinetics (II):
Effect of temperature on reaction rate
& Reaction Mechanisms
Chemical reactions are activated processes.

- We can picture the progress of a chemical reaction in terms of a plot of energy versus reaction co-ordinate (this is a quantity which is a measure of the progress of the reaction along the most energetically facile pathway).
- The reactants R have to climb an uphill energy barrier of height $E^*$ in order to transform into products P.
- The height of this energy barrier can be related to the experimentally determined activation energy $E_A$.
- The greater the quantity of thermal energy supplied, the more easily the energy barrier is surmounted.

Dependence of the rate constant on temperature

<table>
<thead>
<tr>
<th>Exp't</th>
<th>[Ester]</th>
<th>[H₂O]</th>
<th>T (K)</th>
<th>Rate (mol/L·s)</th>
<th>$k$ (L/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.200</td>
<td>288</td>
<td>$1.04 \times 10^{-3}$</td>
<td>0.0521</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.200</td>
<td>298</td>
<td>$2.02 \times 10^{-3}$</td>
<td>0.101</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.200</td>
<td>308</td>
<td>$3.66 \times 10^{-3}$</td>
<td>0.184</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.200</td>
<td>318</td>
<td>$6.46 \times 10^{-3}$</td>
<td>0.332</td>
</tr>
</tbody>
</table>

Can we quantitatively predict the manner in which the rate constant varies with temperature?
Temperature effects in chemical kinetics.

- Chemical reactions are activated processes: they require an energy input in order to occur.
- Many chemical reactions are activated via thermal means.
- The relationship between rate constant \( k \) and temperature \( T \) is given by the empirical Arrhenius equation.
- The activation energy \( E_A \) is determined from experiment, by measuring the rate constant \( k \) at a number of different temperatures. The Arrhenius equation is used to construct an Arrhenius plot of \( \ln k \) versus \( 1/T \). The activation energy is determined from the slope of this plot.

\[
E_A = -R \left( \frac{d \ln k}{d(1/T)} \right) = RT^2 \left( \frac{d \ln k}{dT} \right)
\]

Graphical determination of the activation energy
Using the Arrhenius equation to predict rate constants.

- We can use the Arrhenius equation to predict a rate constant at one temperature, given its value at another temperature if we know the value of the activation energy $E_A$ for the reaction.
- If $k = k_1$ at temperature $T_1$ and $k = k_2$ at temperature $T_2$ and if $T_2 > T_1$ then we can show that

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

- We can also use this expression to obtain the activation energy $E_A$ if the rate constants at two different temperatures are known.

$$E_A = \frac{R \ln \left( \frac{k_2}{k_1} \right)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

A large activation energy signifies a high sensitivity of the reaction rate changes in temperature.

Table 8.4: A factors and activation energies for some first and second order elementary reactions

<table>
<thead>
<tr>
<th>Elementary reaction</th>
<th>$A$</th>
<th>$E_a$/ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order (gas phase)</td>
<td>$/s^{-1}$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CN $\rightarrow$ CH$_3$CN</td>
<td>$5.0 \times 10^{13}$</td>
<td>$+160$</td>
</tr>
<tr>
<td>cyclopropane $\rightarrow$ propene</td>
<td>$1.6 \times 10^{13}$</td>
<td>$+272$</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_2$CH$_3$ $\rightarrow$ C$_6$H$_5$CH$_2^* +$ CH$_3^*$</td>
<td>$7.1 \times 10^{13}$</td>
<td>$+314$</td>
</tr>
<tr>
<td>C$_2$H$_4$ $\rightarrow$ 2 CH$_3^*$</td>
<td>$2.0 \times 10^{17}$</td>
<td>$+365$</td>
</tr>
<tr>
<td>Second order (gas phase)</td>
<td>$/dm^3$ mol$^{-2}$ $s^{-1}$</td>
<td></td>
</tr>
<tr>
<td>CH$_3^<em>$ + CH$_3^</em>$ $\rightarrow$ C$_2$H$_4$</td>
<td>$3.6 \times 10^{10}$</td>
<td>0</td>
</tr>
<tr>
<td>CI$^+$ + O$_3$ $\rightarrow$ CI0 + O$_2$</td>
<td>$1.7 \times 10^{9}$</td>
<td>$+2$</td>
</tr>
<tr>
<td>H$^+$ + F$_2$ $\rightarrow$ HF + F$^*$</td>
<td>$9 \times 10^{5}$</td>
<td>$+10$</td>
</tr>
<tr>
<td>HF + F$^<em>$ $\rightarrow$ H$^</em>$ + F$_2$</td>
<td>$1.3 \times 10^{10}$</td>
<td>$+422$</td>
</tr>
<tr>
<td>Second order (aqueous solution)</td>
<td>$/dm^3$ mol$^{-1}$ $s^{-1}$</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$Br$^- +$ OH$^-$ $\rightarrow$ C$_2$H$_5$OH $+$ Br$^-$</td>
<td>$4.3 \times 10^{11}$</td>
<td>$+90$</td>
</tr>
</tbody>
</table>
Determining the Energy of Activation

**PROBLEM:**

The decomposition of hydrogen iodide,

\[ 2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g) \]

has rate constants of \(9.51 \times 10^{-9} \text{ L mol}^{-1} \text{s}^{-1}\) at 500 K and \(1.10 \times 10^{-5} \text{ L mol}^{-1} \text{s}^{-1}\) at 600 K. Find the activation energy \(E_a\).

**PLAN:**

Use the modification of the Arrhenius equation to find \(E_a\).

\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
E_a = R \ln \frac{k_1}{k_2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}
\]

\[
E_a = -(8.314 \text{J/mol*K}) \ln \left( \frac{1.10 \times 10^{-5}}{9.51 \times 10^{-9}} \frac{1}{1.1 \times 10^{-5}} \right)
\]

\[
E_a = 1.76 \times 10^5 \text{J/mol} = 176 \text{kJ/mol}
\]

---

**Collision theory of bimolecular gas phase reactions.**

- We focus attention on gas phase reactions and assume that chemical reactivity is due to collisions between molecules.
- The theoretical approach is based on the kinetic theory of gases.
- Molecules are assumed to be hard structureless spheres. Hence the model neglects the discrete chemical structure of an individual molecule. This assumption is unrealistic.
- We also assume that no interaction between molecules until contact.
- Molecular spheres maintain size and shape on collision. Hence the centres cannot come closer than a distance \(\delta\) given by the sum of the molecular radii.
- One must have an A,B (or an A,A) encounter over a sufficiently short distance to allow reaction to occur.
- Colliding molecules must have sufficient energy of the correct type to overcome the energy barrier for reaction. A threshold energy \(E^*\) is required.
- The reaction rate will depend on two factors:
  - the number of collisions per unit time (the collision frequency)
  - the fraction of collisions having an energy greater than a certain threshold energy \(E^*\).
SCT: Chemical reactivity related to collisions between reacting molecules.

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

Pre-exponential factor \( A \) related to # collisions per unit time.

**Exponential factor related to fraction of collisions which result in reaction**

*Experiment: Arrhenius equation*

**SCT final results (Chem* p.391)**

\[ k = N_e \sigma \frac{8k_b T}{\pi \mu} \frac{1}{\sqrt{\pi m}} \exp \left( -\frac{E^*}{RT} \right) \]

Efficient collision diameter

\[ \delta = r_A + r_B \]

\[ \sigma = \pi \delta^2 = \pi (r_A + r_B) \]

Area = \( \sigma \)

We compare the results of SCT with the empirical Arrhenius eqn. in order to obtain an interpretation of the activation energy and pre-exponential factor.

\[ k = A_{AB} \exp \left( -\frac{E_A}{RT} \right) \]

\[ k = N_e \sigma \frac{8k_b T}{\pi \mu} \frac{1}{\sqrt{\pi m}} \exp \left( -\frac{E^*}{RT} \right) \]

**SCT predictions**

- The pre-exponential factor should depend on temperature.
- The threshold energy and the activation energy can also be compared.
- Activation energy exhibits a weak T dependence.

Arrhenius

\[ E_A = E^* + \frac{RT}{2} \]

\[ E_A \propto E^* \]
SCT: a summary.

- The major problem with SCT is that the threshold energy $E^*$ is very difficult to evaluate from first principles.
- The predictions of the collision theory can be critically evaluated by comparing the experimental pre-exponential factor with that computed using SCT.
- We define the steric factor $P$ as the ratio between the experimental and calculated $A$ factors.
- We can incorporate $P$ into the SCT expression for the rate constant.
- For many gas phase reactions $P$ is considerably less than unity.
- Typically SCT will predict that $A_{\text{calc}}$ will be in the region $10^{10}$-$10^{11}$ Lmol$^{-1}$s$^{-1}$ regardless of the chemical nature of the reactants and products.
- What has gone wrong? The SCT assumption of hard sphere collision neglects the important fact that molecules possess an internal structure. It also neglects the fact that the relative orientation of the colliding molecules will be important in determining whether a collision will lead to reaction.
- We need a better theory that takes molecular structure into account. The activated complex theory does just that.

\[
P = \frac{A_{\exp}}{A_{\text{calc}}}
\]

\[
k = P_{\text{c,AB}} \exp \left( \frac{-E^*}{RT} \right)
\]

\[
k = P_{\text{c,AB}} \exp \left( \frac{-E^*}{RT} \right)
\]
Consecutive Reactions.

- Mother / daughter radioactive decay.

\[ ^{218}Pb \rightarrow ^{214}Pb \rightarrow ^{214}Bi \]

\[ k_1 = 5 \times 10^{-3} \text{s}^{-1}, \quad k_2 = 6 \times 10^{-4} \text{s}^{-1} \]

For these consecutive reactions, the rate of change of intermediate species \( X \) is given by the coupled LDEs:

\[
\begin{align*}
\frac{da}{dt} & = -k_1 a \\
\frac{dx}{dt} & = k_1 a - k_2 x \\
\frac{dp}{dt} & = k_2 x
\end{align*}
\]

Mass balance requires that:

\[ p = a_0 - a - x \]

Hence once \( a(t) \) and \( x(t) \) are evaluated we can determine \( p(t) \).

The solutions to the coupled equations are:

\[
\begin{align*}
a(t) & = a_0 e^{-k_1 t} \\
x(t) & = \frac{k_1 a_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \\
p(t) & = a_0 - a_0 e^{-k_1 t} - \frac{k_2 a_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right)
\end{align*}
\]

We different behaviour depending on the ratio of the rate constants \( k_1 \) and \( k_2 \).

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Consecutive reactions: Rapid decay of intermediate.

Intermediate \( X \) is fairly reactive. Concentration of intermediate \( X \) will be small at all times.

\[ A \xrightarrow{k_1} X \xrightarrow{k_2} P \]

Can use Quasi-Steady State Approximation QSSA under these Conditions.

Rate of change of concentration of intermediate species \( X \) with respect to time is zero.

\[ \frac{dx}{dt} = R_{X,\text{formation}} - R_{X,\text{removal}} = 0 \]

\[ t = \frac{1}{k_1} \]

\[ k_2 = 0.1 k_1 \]
Consecutive reactions:
Slow decay of intermediate.

\[ u = \frac{a}{a_0} \]
\[ v = \frac{x}{a_0} \]
\[ w = \frac{p}{a_0} \]

Initial reactant A more reactive than intermediate X.

Rate determining step in a consecutive reaction is the step that is associated with the highest energy barrier and is therefore kinetically limiting and determines the net reaction rate.

Rate Determining Step

\[ k_1 \gg k_2 \]

\[ A \xrightarrow{k_1} X \xrightarrow{k_2} P \]

Fast \quad Slow

* Reactant A decays rapidly, concentration of intermediate species X is high for much of the reaction and product P concentration rises gradually since X → P transformation is slow.

\[ k_2 \gg k_1 \]

Rate Determining Step

\[ A \xrightarrow{k_1} X \xrightarrow{k_2} P \]

Slow \quad Fast

* Reactant A decays slowly, concentration of intermediate species X will be low for the duration of the reaction and to a good approximation the net rate of change of intermediate concentration with time is zero. Hence the intermediate will be formed as quickly as it is removed. This is the quasi steady state approximation (QSSA).
**Rate Determining Steps (I).**

Case I.

\[ k' = \frac{k_2}{k_1} \]

\[ k_2 \gg k_1 \]

\[ k = \frac{k_2}{k_1} \]

\[ k_2 \gg k_1 \]

\[ \Delta G_1^\ddagger \gg \Delta G_{II}^\ddagger \]

Step I is rate determining since it has the highest activation energy barrier.

**Rate Determining Steps (II).**

Case II.

\[ k' = \frac{k_2}{k_1} \]

\[ k_2 \ll k_1 \]

\[ k = \frac{k_2}{k_1} \]

\[ k_2 \ll k_1 \]

\[ \Delta G_1^\ddagger \ll \Delta G_{II}^\ddagger \]

Step II is rate determining since it has the highest activation energy barrier.

**Key Parameter**

\[ k = \frac{k_2}{k_1} \]

**Intermediate X fairly reactive.**

\[ [X] \] will be small at all times.

The reactant species A will be more reactive than the intermediate X.
Activated Complex Theory (ACT) of chemical reaction kinetics.

Progress of a chemical reaction can be expressed in terms of a plot of energy versus reaction co-ordinate. The reaction coordinate may be described in terms of changes in particular bond lengths since these will vary as the reaction progresses.

**Potential Energy Surfaces 1**

A reaction surface is a plot of the energy of a reaction system as a function of all the independent variables (bond lengths and bond angles). Even a collinear triatomic reaction such as

\[ A + BC \rightarrow AB + C \]

needs a 3-D plot:

\[ E \]

\[ r_{AB}, r_{AC}, r_{BC} \]

or a contour plot:

minimum energy path

symmetry vibration of \( \Delta R \)

Henry Eyring 1901-1981

Developed (in 1935) the Transition State Theory (TST) or Activated Complex Theory (ACT) of Chemical Kinetics.
Potential energy surface for a chemical reaction

\[ A + BC \rightarrow [ABC]^* \rightarrow AB + C \]

- Calculate potential energy \( V \) of System \( A(g) + BC(g) \rightarrow AB(g) + C(g) \).
- For a fixed angle of approach \( \theta \) between reactants \( (\theta = 180^\circ) \) we plot \( V \) versus \( R_{AB} \) and \( R_{BC} \) to define a 3D potential energy surface.
- This defines a detailed map of the trajectory of the system as it proceeds from the initial reactant state to the final product state.
- This procedure is very computationally intensive and has only been carried out for fairly simple reactions in the gas phase.

Transition state theory (TST) or activated complex theory (ACT).

- In a reaction step as the reactant molecules \( A \) and \( B \) come together they distort and begin to share, exchange or discard atoms.
- They form a loose structure \( AB^\ddagger \) of high potential energy called the activated complex that is poised to pass on to products or collapse back to reactants \( C + D \).
- The peak energy occurs at the transition state. The energy difference from the ground state is the activation energy \( E_a \) of the reaction step.
- The potential energy falls as the atoms rearrange in the cluster and finally reaches the value for the products.
- Note that the reverse reaction step also has an activation energy, in this case higher than for the forward step.
Transition state theory

• The theory attempts to explain the size of the rate constant \( k_r \) and its temperature dependence from the actual progress of the reaction (reaction coordinate).
• The progress along the reaction coordinate can be considered in terms of the approach and then reaction of an H atom to an \( \text{F}_2 \) molecule.
• When far apart the potential energy is the sum of the values for H and \( \text{F}_2 \).
• When close enough their orbitals start to overlap
  - A bond starts to form between H and the closer F atom \( \text{H} \cdot \cdot \cdot \text{F} \).
  - The \( \text{F} \cdot \cdot \cdot \text{F} \) bond starts to lengthen.
• As H becomes closer still the \( \text{H} \cdot \cdot \cdot \text{F} \) bond becomes shorter and stronger and the \( \text{F} \cdot \cdot \cdot \text{F} \) bond becomes longer and weaker.
  - The atoms enter the region of the activated complex.
• When the three atoms reach the point of maximum potential energy (the transition state) a further infinitesimal compression of the \( \text{H} \cdot \cdot \cdot \text{F} \) bond and stretch of the \( \text{F} \cdot \cdot \cdot \text{F} \) bond takes the complex through the transition state.

Thermodynamic approach

\[
\begin{align*}
  \text{A} + \text{B} & \xrightleftharpoons{K^\ddagger} \text{activated complex AB}^\ddagger \xrightarrow{k^\ddagger} \text{products} \quad \text{where } K^\ddagger = \frac{[\text{AB}^\ddagger]}{[\text{A}][\text{B}]}
\end{align*}
\]

• Therefore rate of formation of products = \( k^\ddagger [\text{AB}^\ddagger] = k^\ddagger K^\ddagger [\text{A}][\text{B}] \).
• Compare this expression to the rate law: \( \text{rate of formation of products} = k_r [\text{A}][\text{B}] \).
• Hence the rate constant \( k_r = k^\ddagger K^\ddagger \).
• The Gibbs energy for the process is given by \( \Delta^\ddagger \mathcal{G} = -RT \ln (K^\ddagger) \) and so \( K^\ddagger = \exp(\Delta^\ddagger \mathcal{G} / RT) \).
• Hence rate constant \( k_r = k^\ddagger \exp(\Delta^\ddagger \mathcal{G} / RT) \).
• This expression has the same form as the Arrhenius expression.
  - The activation energy \( E_a \) relates to \( \Delta^\ddagger \mathcal{H} \).
  - Pre-exponential factor \( A = k^\ddagger \exp(\Delta^\ddagger S / R) \).
  - The steric factor \( P \) can be related to the change in disorder at the transition state.
Advantages of transition state theory

• Provides a complete description of the nature of the reaction including
  - the changes in structure and the distribution of energy through the transition state
  - the origin of the pre-exponential factor $A$ with units $t^{-1}$ that derive from frequency or velocity
  - the meaning of the activation energy $E_a$
• Rather complex fundamental theory can be expressed in an easily understood pictorial diagram of the transition state - plot of energy vs the reaction coordinate
• The pre-exponential factor $A$ can be derived a priori from statistical mechanics in simple cases
• The steric factor $P$ can be understood as related to the change in order of the system and hence the entropy change at the transition state
• Can be applied to reactions in gases or liquids
• Allows for the influence of other properties of the system on the transition state (e.g., solvent effects).

Disadvantage

• Not easy to estimate fundamental properties of the transition state except for very simple reactions
  - theoretical estimates of $A$ and $E_a$ may be 'in the right ball-park' but still need experimental values