Course Summary.

- Contact short but sweet. 5 Lectures in total (4 this week, 1 next week, 3 tutorials next week).
- We revise quantitative aspects of JF kinetics and discuss some new more advanced topics and introduce the mathematical theory of chemical kinetics.
- Topics include:
  - **Lecture 3, 4.** Enzyme kinetics (Michaelis-Menten case) and surface reactions involving adsorbed reactants (Langmuir adsorption isotherm).
  - **Lecture 5.** Theory of chemical reaction rates: bimolecular reactions. Simple Collision Theory & Activated Complex Theory.
Recommended reading.

- Burrows et al Chemistry³, OUP Chapter 8, pp.339-403.
  - Both of these books by well established authors are clearly written with an excellent style and both provide an excellent basic treatment of reaction kinetics with emphasis on biological examples. These books are set at just the right level for the course and you should make every effort to read the recommended chapters in detail. Also the problem sheets will be based on problems at the end of these chapters!
  - A more advanced and complete account of the course material. Much of chapter 24 is JS material.
  - Modern textbook providing a complete account of modern chemical reaction kinetics. Good on experimental methods and theory.
  - Another modern kinetics textbook which does as it states in the title, i.e. provide a readable introduction to the subject! Well worth browsing through.
Reaction Rate: The Central Focus of Chemical Kinetics

The wide range of reaction rates.

1 femtosecond (fs) = $10^{-15}$ s = $1/10^{15}$ s!
Reactions studies under constant temperature conditions.  
Mixing of reactants must occur more rapidly than reaction occurs.  
Start of reaction pinpointed accurately.  
Method of analysis must be much faster than reaction itself.

**Chemical reaction kinetics.**

- Chemical reactions involve the forming and breaking of chemical bonds.  
- Reactant molecules (H₂, I₂) approach one another and collide and interact with appropriate energy and orientation. Bonds are stretched, broken and formed and finally product molecules (HI) move away from one another.  
- How can we describe the rate at which such a chemical transformation takes place?  

\[ H_2(g) + I_2(g) \rightarrow 2HI(g) \]

- Thermodynamics tells us all about the energetic feasibility of a reaction: we measure the Gibbs energy ΔG for the chemical Reaction.  
- Thermodynamics does not tell us how quickly the reaction will proceed: it does not provide kinetic information.
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.

- 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.

\[
R_{\Sigma} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}
\]

Net reaction rate
Units: mol dm\(^{-3}\) s\(^{-1}\)
Geometric definition of reaction rate.

Rate expressed as tangent line to concentration/time curve at a particular time in the reaction.

Reaction Rates and Reaction Stoichiometry

\[ \text{O}_3(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \]

\[
\text{rate} = -\frac{d[\text{O}_3]}{dt} = -\frac{d[\text{NO}]}{dt} = +\frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{O}_2]}{dt}
\]

Reaction rate can be quantified by monitoring changes in either reactant concentration or product concentration as a function of time.
2 \text{H}_2\text{O}_2 \text{(aq)} \rightarrow 2 \text{H}_2\text{O} \text{(l)} + \text{O}_2 \text{(g)}

The general case.

• Why do we define our rate in this way?
  – removes ambiguity in the measurement of reaction rates in that we now obtain a single rate for the entire equation, not just for the change in a single reactant or product.

\[ aA + bB \rightarrow pP + qQ \]

\[
\text{Rate } R = \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = + \frac{1}{q} \frac{d[Q]}{dt} = + \frac{1}{p} \frac{d[P]}{dt}
\]
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 changes as the reaction proceeds.

$$R_j = \frac{1}{v_j} \lim_{\Delta t \to 0} \frac{\Delta [J]}{\Delta t} = \frac{1}{v_j} \frac{d[J]}{dt}$$

2$H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

$$R = \frac{1}{2} \frac{d[H_2]}{dt} - \frac{1}{2} \frac{d[O_2]}{dt} - \frac{1}{2} \frac{d[H_2O]}{dt}$$

Note: Units of rate: concentration/time, hence $R_j$ has units mol dm$^{-3}$s$^{-1}$. $v_j$ denotes the stoichiometric coefficient of species $J$. If $J$ is a reactant $v_j$ is negative and it will be positive if $J$ is a product species.

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.

Reaction rate and reaction order.

- 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 changes (decreases) 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.
- Hence in other words:
  - the reaction order is a measure of the sensitivity of the reaction rate to changes in the concentration of the reactants.
Initial rate determined by evaluating tangent to concentration versus time curve at a given time $t_0$. 

\[ 2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \]

$T = 338 \text{ K}$

Initial rate is proportional to initial concentration of reactant.

\[ \text{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5] \]

Rate constant $k = 5.2 \times 10^{-3} \text{ s}^{-1}$

Working out a rate equation.

Reaction order determination.


Log $R$ \hspace{1cm} Slope $= \alpha$ \hspace{1cm} Log $[A]$ 

Log $R$ \hspace{1cm} Slope $= \beta$ \hspace{1cm} Log $[B]$
Different rate equations imply different mechanisms.

\[ H_2 + I_2 \rightarrow 2HI \]
\[ R = \frac{d[H]}{dt} = k[H_2][I_2] \]

\[ H_2 + Br_2 \rightarrow 2HBr \]
\[ R = \frac{d[HBr]}{dt} = k[H_2][Br_2]^{1/2} \left(1 + \frac{k[HBr]}{[Br_2]}\right) \]

\[ H_2 + Cl_2 \rightarrow 2HCl \]
\[ R = \frac{d[HCl]}{dt} = k[H_2][Cl_2]^{1/2} \]

- The rate law provides an important guide to reaction mechanism, since any proposed mechanism must be consistent with the observed rate law.
- A complex rate equation will imply a complex multistep reaction mechanism.
- Once we know the rate law and the rate constant for a reaction, we can predict the rate of the reaction for any given composition of the reaction mixture.
- We can also use a rate law to predict the concentrations of reactants and products at any time after the start of the reaction.

**Integrated rate equation.**

Many rate laws can be cast as differential equations which may then be solved (integrated) using standard methods to finally yield an expression for the reactant or product concentration as a function of time.

We can write the general rate equation for the process \( A \rightarrow \text{Products} \) as

\[ \frac{dc}{dt} = kF(c) \]

where \( F(c) \) represents some distinct function of the reactant concentration \( c \). One common situation is to set \( F(c) = c^n \) where \( n = 0, 1, 2, \ldots \) and the exponent \( n \) defines the reaction order wrt the reactant concentration \( c \).

The differential rate equation may be integrated once to yield the solution \( c = c(t) \) provided that the initial condition at zero time which is \( c = c_0 \) is introduced.
Zero order kinetics. The reaction proceeds at the same rate $R$ regardless of concentration.

Rate equation:

$$ R = \frac{dc}{dt} = k $$

$c = c_0$ when $t = 0$

integrate using initial condition

$$ c(t) = -kt + c_0 $$

diagnostic plot

slope = $-k$

First order kinetics.

First order differential rate equation.

$$ -\frac{dc}{dt} = kc $$

Initial condition

$$ t = 0 \quad c = c_0 $$

Solve differential equation

Via separation of variables

First order reaction

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

Reactant concentration as function of time.

Zero order kinetics.

First order kinetics.

First order reaction

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

Molar concentration of reactant, $[A]_0$

- $k \rightarrow s^{-1}$
- $k$ small
- $k$ large

$c(t) = c_0 e^{-kt} = c_0 e^{-\theta}$
$u = \frac{c(t)}{c_0} = e^{-\frac{\theta}{k}}$
$\theta = kt$

Half life $\tau_{1/2}$

- $\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$
- $\tau_{1/2} = \frac{\ln 2}{\frac{c_0}{2}}$ ($u = 1/2$)

Mean lifetime of reactant molecule

$$\tau = \frac{1}{c_0} \int_0^\infty c(t) dt = \frac{1}{c_0} \int_0^\infty c_0 e^{-u} du = \frac{1}{k}$$

First order kinetics: half life.

In each successive period of duration $\tau_{1/2}$, 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.

- $u = \frac{a}{a_0}$
- $t = \tau_{1/2}$, $c = c_0 / 2$
- $\tau_{1/2} = \ln 2 / k = 0.693 / k$
Second order kinetics: equal reactant concentrations.

$$\frac{dc}{dt} = kc^2$$

separate variables
integrate

$$\frac{1}{c} = kt + \frac{1}{c_0}$$

half life

$$t = \frac{1}{k}c$$

rate varies as square of reactant concentration

$$c(t) = \frac{c_0}{1 + kc_0t}$$

dm^3\text{mol}^{-1}\text{s}^{-1}

slope = k

rate varies as square of reactant concentration

$2A \rightarrow P$

$1$ kmol

$2$

$0$

t

$c_0$

rate

slope

$1/2$

$0$

$1/2$

$0$

$1/2$

$0$

$1/2$

$0$

$1$

$1$

$kc$

as $c_0$ increases

rate

$1$

$1$

$kc$

as $c_0$ increases

rate

1st order kinetics

$$u(\theta) = e^{-k\theta}$$

$$c(t) = c_0e^{-kt}$$

$1$

$0$

$0$

$1$

$k$ increasing

Time, $t$

$\theta = kt$

2nd order kinetics

$$u(\theta) = \frac{1}{1 + \theta}$$

$$c(t) = \frac{c_0}{1 + kc_0t}$$

$1$

$0$

$0$

$1$

$k$ increasing

Time, $t$

$\theta = kc_0t$
**1st and 2nd order kinetics: Summary.**

<table>
<thead>
<tr>
<th>Reaction Differential rate equation</th>
<th>Concentration variation with time</th>
<th>Diagnostic Equation</th>
<th>Half Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A \xrightarrow{k} \text{Products}$</td>
<td>$\frac{dc}{dt} = kc$</td>
<td>$c(t) = c_0 \exp[-kt]$</td>
<td>$t_{1/2} = \frac{\ln 2}{k}$</td>
</tr>
<tr>
<td>$2A \xrightarrow{k} \text{Products}$</td>
<td>$\frac{dc}{dt} = k_c c^2$</td>
<td>$c(t) = \frac{1}{k} \frac{1}{1 + k_c c_0}$</td>
<td>$t_{1/2} = \frac{1}{k_c c_0}$</td>
</tr>
</tbody>
</table>

**Differential rate equation:**

**Concentration variation with time:**

**Diagnostic Equation:**

**Half Life:**

**1st order plots:**
- **Slope = -$k_1$**
- **$1/c(t)$**
- **$t$**

**2nd order plots:**
- **Slope = $k_2$**
- **$c_0$**
- **$t$**

**Diagnostic plots:**

**Half life**

- $t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k c_0^{n-1}}$
- $\ln t_{1/2} = \ln \left[ \frac{2^{n-1} - 1}{(n-1)k} \right] - (n-1) \ln c_0$

**Half life**

- $t_{1/2} \propto c_0^{2-n}$
- $n > 1 \Rightarrow t_{1/2} \downarrow \text{as } c_0 \uparrow$
- $n < 1 \Rightarrow t_{1/2} \uparrow \text{as } c_0 \uparrow$

**Slope:**

- $\text{slope} = -(n-1)k$
- $\text{slope} = -(n-1)$

**n th order kinetics: equal reactant concentrations.**

- $\frac{dc}{dt} = k c^n$
- separate variables integrate
- $n \neq 1$
- $n = 0, 2, 3, \ldots$

**Rate constant $k$ obtained from slope.**

**reaction order $n$ determined from slope.**

**nA $\xrightarrow{k} P$**

**Half life**

- $t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k c_0^{n-1}}$
- $\ln t_{1/2} = \ln \left[ \frac{2^{n-1} - 1}{(n-1)k} \right] - (n-1) \ln c_0$
### Summary of kinetic results.

**Rate equation**

\[ nA \xrightarrow{k} P \]

- \( t = 0 \quad c = c_0 \)
- \( t = \tau_{1/2} \quad c = \frac{c_0}{2} \)

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>( R = -\frac{dc}{dt} )</th>
<th>Integrated expression</th>
<th>Units of ( k )</th>
<th>Half life ( \tau_{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( k )</td>
<td>( e(t) = -kt + c_0 )</td>
<td>mol dm(^{-3})s(^{-1})</td>
<td>( \frac{c_0}{2k} )</td>
</tr>
<tr>
<td>1</td>
<td>( kc )</td>
<td>( \ln \left( \frac{c_0}{c(t)} \right) = kt )</td>
<td>s(^{-1})</td>
<td>( \ln \frac{2}{k} )</td>
</tr>
<tr>
<td>2</td>
<td>( kc^2 )</td>
<td>( \frac{1}{c(t)} = kt + \frac{1}{c_0} )</td>
<td>dm(^{3})mol(^{-1})s(^{-1})</td>
<td>( \frac{1}{kc_0} )</td>
</tr>
<tr>
<td>3</td>
<td>( kc^3 )</td>
<td>( \frac{1}{c(t)} = 2kt + \frac{1}{c_0} )</td>
<td>dm(^{4})mol(^{-1})s(^{-1})</td>
<td>( \frac{3}{2kc_0} )</td>
</tr>
<tr>
<td>( n )</td>
<td>( kc^n )</td>
<td>( \frac{1}{c(t)} = (n-1)kt + \frac{1}{c_0} )</td>
<td></td>
<td>( \frac{1}{n-1} \left( \frac{2^{n-1} - 1}{kc_0^{n-1}} \right) )</td>
</tr>
</tbody>
</table>

**Second order kinetics:**

Unequal reactant concentrations.

**rate equation**

\[ R = -\frac{da}{dt} = -\frac{db}{dt} = \frac{dp}{dt} = kab \]

**initial conditions**

\( t = 0 \quad a = a_0 \quad b = b_0 \quad a_0 \neq b_0 \)

integrate using partial fractions

\[ F(a, b) = \frac{1}{b_0 - a_0} \left( \ln \left( \frac{b/b_0}{a/a_0} \right) \right) = kt \]

**half life**

\[ \tau_{1/2} = \frac{\ln \left( \frac{2}{\zeta} \right)}{ka_0(\zeta - 1)} \]

- \( \zeta = \frac{b_0}{a_0} \)
- \( \zeta \gg 1 \quad \frac{1}{\zeta} \to 0 \)
- \( \tau_{1/2} \approx \frac{\ln 2}{kh_a} = \frac{\ln 2}{k'} \)
- \( k' = kh_b \)

**Pseudo first order kinetics** when \( b_0 \gg a_0 \)

- slope = \( k \)
- pseudo 1st order rate constant
Temp Effects in Chemical Kinetics.


Van’t Hoff expression:

\[
\left( \frac{d \ln K}{dT} \right)_p = \frac{\Delta U^0}{RT^2}
\]

Standard change in internal energy:

\[
\Delta U^0 = E - E'
\]

This leads to formal definition of Activation Energy.

\[
\text{Temperature effects in chemical kinetics.}
\]

- 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.

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

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

\[
\text{Slope} = -\frac{E_A}{R}
\]

Pre-exponential factor
Temperature dependence of rate constants

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

- Empirical theory of Arrhenius gives a useful way to parameterize rate constants
  - \( A \) ≡ pre-exponential factor
  - \( E_a \) ≡ activation energy
- Often seen in analysis of kinetic data

Non-Arrhenius behavior

- Arrhenius behavior is empirical
- For some reactions the temperature dependence of the rate constant is not exponential
- Theory does not easily predict Arrhenius form
- Amazing that Arrhenius behavior is so often seen
In some circumstances the Arrhenius Plot is curved which implies that the Activation energy is a function of temperature. Hence the rate constant may be expected to vary with temperature according to the following expression.

\[ k = a T^m \exp\left(-\frac{E}{RT}\right) \]

We can relate the latter expression to the Arrhenius parameters \(A\) and \(E_A\) as follows.

\[ \ln k = \ln a + m \ln T - \frac{E}{RT} \]

\[ E_A = RT \left( \frac{d \ln k}{dT} \right) = RT \left( \frac{m}{T} + \frac{E}{RT} \right) = E + mRT \]

Hence

\[ k = a T^m e^e \exp\left(-\frac{E_A}{RT}\right) \]

\[ A = a T^m e^e \exp\left(-\frac{E_A}{RT}\right) \]

Consecutive Reactions.

- Mother / daughter radioactive decay.

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

\( k_1 = 5 \times 10^{-3} \, \text{s}^{-1} \) \( k_2 = 6 \times 10^{-4} \, \text{s}^{-1} \)

3 coupled LDE’s define system:

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

Mass balance requirement:

\[ p = a_0 - a - x \]

The solutions to the coupled equations are:

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

We get different kinetic behaviour depending on the ratio of the rate constants \(k_1\) and \(k_2\)
Consecutive reaction: Case I.
Intermediate formation fast, intermediate decomposition slow.

Case I.
\[ \kappa = \frac{k_2}{k_1} \ll 1 \]
\[ k_2 \ll k_1 \]

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

I: fast
II: slow rds

\[ \Delta G_{I}^{\dagger} \ll \Delta G_{II}^{\dagger} \]

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

The reactant species A will be more reactive than the intermediate X.

Initial reactant A more reactive than intermediate X.

Concentration of intermediate significant over time course of reaction.
Consecutive reactions Case II:
Intermediate formation slow, intermediate decomposition fast.

Case II. \[ \kappa = \frac{k_2}{k_1} \]

Intermediate X fairly reactive. [X] will be small at all times.

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

Intermediate concentration is approximately constant after initial induction period.
Parallel reaction mechanism.

- We consider the kinetic analysis of a concurrent or parallel reaction scheme which is often met in real situations.
- A single reactant species can form two distinct products.
- We assume that each reaction exhibits 1st order kinetics.
- Initial condition: \( t=0, a=a_0; x=0, y=0 \)
- Rate equation:

\[
R = -\frac{da}{dt} = k_1a + k_2a = (k_1 + k_2)\frac{a}{2}
\]

\[
a(t) = a_0 \exp[-k_1t] = a_0 \exp[-(k_1 + k_2)t]
\]

- Half life:

\[
\tau_{1/2} = \frac{\ln 2}{k_2} = \frac{\ln 2}{k_1 + k_2}
\]

- All of this is just an extension of simple 1st order kinetics.

Final product analysis yields rate constant ratio.

\[
\lim_{t \to \infty} \frac{x(t)}{y(t)} = \frac{k_1}{k_2}
\]
Parallel Mechanism: $k_1 >> k_2$

Theory

\[ \kappa = \frac{k_2}{k_1} = 0.1 \]

\[ \frac{k_2}{k_1} = 10 = \frac{v(x)}{w(x)} \]

Parallel Mechanism: $k_2 >> k_1$

Theory

\[ \kappa = \frac{k_2}{k_1} = 10 \]

\[ \frac{k_1}{k_2} = 0.1 = \frac{v(x)}{w(x)} \]
Reaching Equilibrium on the Macroscopic and Molecular Level

Chemical Equilibrium: a kinetic definition.

- Countless experiments with chemical systems have shown that in a state of equilibrium, the concentrations of reactants and products no longer change with time.
- This apparent cessation of activity occurs because under such conditions, all reactions are microscopically reversible.
- We look at the dinitrogen tetroxide/nitrogen oxide equilibrium which occurs in the gas phase.

\[
\begin{align*}
\text{Kinetic analysis: } & \quad \frac{d\left[N_2O_4\right]}{dt} = -2 \frac{d[NO_2]}{dt} \\
R &= k[NO_2], \quad \frac{d[NO_2]}{dt} = -k[N_2O_4] \\
\text{Validity for any time } t
\end{align*}
\]

\[
\text{Equilibrium: } \quad \frac{k[N_2O_4]}{[NO_2]} = \frac{k}{k} = K
\]

Concentrations vary with time

Concentrations time invariant

Valid for any time \( t \)
First order reversible reactions: understanding the approach to chemical equilibrium.

Rate equation

\[ \frac{da}{dt} = -ka + k'b \]

Initial condition

\[ t = 0 \quad a = a_0 \quad b = 0 \]

Mass balance condition

\[ \forall t \quad a + b = a_0 \]

Rate equation in normalised form

\[ \frac{du}{d\tau} + u = \frac{1}{1 + \theta} \]

Solution produces the concentration expressions

\[ u(\tau) = \frac{1}{1 + \theta} \left[ 1 + \theta \exp[-\tau] \right] \]
\[ v(\tau) = \frac{\theta}{1 + \theta} \left[ 1 - \exp[-\tau] \right] \]

Introduce normalised variables.

\[ u = \frac{a}{a_0} \quad v = \frac{b}{a_0} \quad \tau = (k + k')t \quad \theta = \frac{k}{k'} \]

Reaction quotient \( Q \)

\[ Q(\tau) = \frac{v(\tau)}{u(\tau)} = \theta \left[ \frac{1 - \exp[-\tau]}{1 + \theta \exp[-\tau]} \right] \]

First order reversible reactions: approach to equilibrium.

![Graph showing concentration vs \( \tau = (k+k')t \) for Reactant A and Product B, reaching equilibrium at \( K = Q(\tau \to \infty) = \frac{v(\infty)}{u(\infty)} \).]
Understanding the difference between reaction quotient $Q$ and Equilibrium constant $K$.

Approach to Equilibrium $Q < \theta$

Equilibrium $Q = K = \theta$

\[ Q(\tau) = \frac{v(\tau)}{u(\tau)} = \theta \frac{1 - \exp[-\tau]}{1 + \theta \exp[-\tau]} \]

As $t \to \infty$, $Q \to K = \theta = \frac{k}{k'}$

Kinetic versus Thermodynamic control.

- In many chemical reactions, the competitive formation of side products is a common and often unwanted phenomenon.
- It is often desirable to optimize the reaction conditions to maximize selectivity and hence optimize product formation.
- **Temperature** is often a parameter used to modify selectivity.
- Operating at low temperature is generally associated with the idea of high selectivity (this is termed **kinetic** control). Conversely, operating at high temperature is associated with low selectivity and corresponds to **Thermodynamic** control.
- **Time** is also an important parameter. At a given temperature, although the kinetically controlled product predominates at short times, the thermodynamically controlled product will predominate if the reaction time is long enough.

Refer to JCE papers dealing with this topic given as extra handout.
Assume that reaction product $P_1$ is less stable than the product $P_2$. Also its formation is assumed to involve a lower activation energy $E_{A_1}$.

**Temperature effect.**

**Kinetic control.**
- Assume that energy of products $P_1$ and $P_2$ are much lower than that of the reactant $R$ then $E_{A,1} < E_{A,2}$ and $E_{A,1} = E_{A,2}$.
- At low temperature one neglects the fraction of molecules having an energy high enough to re-cross the energy barrier from products to reactants.
- Under such conditions the product ratio $[P_1]/[P_2]$ is determined only by the activation barriers for the forward $R \rightarrow P$ reaction steps.

**Thermodynamic control.**
- At high temperature the available thermal energy is considered large enough to assume that energy barriers are easily crossed. Thermodynamic equilibrium is reached and the product ratio $[P_1]/[P_2]$ is now determined by the relative stability of the products $P_1$ and $P_2$.

$$
\frac{[P_1]}{[P_2]} = K_1^{k_1} = \exp \left[ -\frac{\Delta G^0_i}{RT} \right]
$$

$$
\frac{[P_1]}{[P_2]} = \frac{k_1}{k_2} = \exp \left[ -\frac{\Delta G^0_i - \Delta G^0_j}{RT} \right]
$$
\[
\frac{d[R]}{dt} = (k_1 + k_2) [R] - k_1 [P_1] - k_2 [P_2]
\]
\[
\frac{d[P_1]}{dt} = k_2 [R] - k_1 [P_1]
\]
\[
\frac{d[P_2]}{dt} = k_1 [R] - k_2 [P_2]
\]

**Short time approximation.**

Neglect \(k_1\), \(k_2\) terms.

\[
[R] = [R]_0 e^{-(k_1 + k_2)t}
\]
\[
[P_1] = \frac{k_2 [R]_0}{k_1 + k_2} e^{-(k_1 + k_2)t}
\]
\[
[P_2] = \frac{k_1 [R]_0}{k_1 + k_2} e^{-(k_1 + k_2)t}
\]

General solution valid for intermediate times.

\[
[R] = [R]_0 \left\{ \frac{k_1 k_2}{\lambda_1 \lambda_2} + \frac{(\lambda_1 + k_2) (\lambda_1 + k_1)}{\lambda_1 (\lambda_1 - \lambda_2)} \exp[\lambda_1 t] + \frac{(\lambda_2 + k_1) (\lambda_2 + k_2)}{\lambda_2 (\lambda_2 - \lambda_1)} \exp[\lambda_2 t] \right\}
\]
\[
[P_1] = [R]_0 \left\{ \frac{k_2}{\lambda_1 \lambda_2} + \frac{k_1 (\lambda_1 + k_2)}{\lambda_1 (\lambda_1 - \lambda_2)} \exp[\lambda_1 t] + \frac{k_2 (\lambda_2 + k_1)}{\lambda_2 (\lambda_2 - \lambda_1)} \exp[\lambda_2 t] \right\}
\]
\[
[P_2] = [R]_0 \left\{ \frac{k_1}{\lambda_1 \lambda_2} + \frac{k_1 (\lambda_1 + k_1)}{\lambda_1 (\lambda_1 - \lambda_2)} \exp[\lambda_1 t] + \frac{k_2 (\lambda_2 + k_2)}{\lambda_2 (\lambda_2 - \lambda_1)} \exp[\lambda_2 t] \right\}
\]

\[
\lambda_{1,2} = \frac{-\beta \pm \sqrt{\beta^2 - 4\gamma}}{2} = \frac{-\beta}{2} \left\{ 1 \pm \sqrt{1 - \frac{4\gamma}{\beta^2}} \right\}
\]

\[
\beta = k_1 + k_2 + k_{-1} + k_{-2}
\]
\[
\gamma = k_1 k_{-2} + k_{-1} k_2 + k_{-1} k_{-2}
\]

These expressions reproduce the correct limiting forms corresponding to kinetic and Thermodynamic control in the limits of short and long time respectively.
Detailed mathematical analysis of complex reaction mechanisms is difficult. Some useful methods for solving sets of coupled linear differential rate equations include matrix methods and Laplace Transforms. In many cases utilisation of the quasi steady state approximation leads to a considerable simplification in the kinetic analysis.

Mathematically, QSSA implies

\[
\frac{dx}{dt} = R_X \text{formation} - R_X \text{removal} \approx 0
\]

\[
R_X \text{formation} = R_X \text{removal}
\]

The QSSA assumes that after an initial induction period (during which the concentration \(x\) of intermediates \(X\) rise from zero), and during the major part of the reaction, the rate of change of concentrations of all reaction intermediates are negligibly small.

Consecutive reactions \(k_1 = 0.1 k_2\).

QSSA: a fluid flow analogy.

- QSSA illustrated via analogy with fluid flow.
- If fluid level in tank is to remain constant then rate of inflow of fluid from pipe 1 must balance rate of outflow from pipe 2.
- Reaction intermediate concentration equivalent to fluid level. Inflow rate equivalent to rate of formation of intermediate and outflow rate analogous to rate of removal of intermediate.
Consecutive reaction mechanisms.

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

Step I is reversible, step II is irreversible.

Rate equations

\[
\begin{align*}
\frac{du}{d\tau} &= -u + \kappa v \\
\frac{dv}{d\tau} &= u - (\kappa + \phi) v \\
\frac{dw}{d\tau} &= \phi v
\end{align*}
\]

Coupled LDE’s can be solved via Laplace Transform or other methods.

\[
\begin{align*}
u(\tau) &= \frac{1}{\beta - \alpha} \left( (\kappa + \phi - \alpha) \exp[-\alpha \tau] - (\kappa + \phi - \beta) \exp[-\beta \tau] \right) \\
v(\tau) &= \frac{1}{\beta - \alpha} \left( \exp[-\alpha \tau] - \exp[-\beta \tau] \right) \\
w(\tau) &= 1 - \frac{1}{\beta - \alpha} \left( \beta \exp[-\alpha \tau] - \alpha \exp[-\beta \tau] \right)
\end{align*}
\]

Definition of normalised variables and initial condition.

Note that \( \alpha \) and \( \beta \) are composite quantities containing the individual rate constants.

\[
\begin{align*}
\alpha &= \phi \\
\beta &= 1 + \kappa + \phi
\end{align*}
\]

QSSA assumes that

\[
\frac{dv}{d\tau} \approx 0
\]

\[
\begin{align*}
u_{ss} &= \frac{u_{ss}}{\kappa + \phi} \\
v_{ss} &= 1 - \frac{1}{\beta - \alpha} \left( \beta \exp[-\alpha \tau] - \alpha \exp[-\beta \tau] \right)
\end{align*}
\]

Using the QSSA we can develop more simple rate equations which may be integrated to produce approximate expressions for the pertinent concentration profiles as a function of time. The QSSA will only hold provided that:

- the concentration of intermediate is small and effectively constant, and so:
  - the net rate of change in intermediate concentration wrt time can be set equal to zero.

\[
\begin{align*}
\frac{dv_{ss}}{d\tau} &= \frac{\phi}{\kappa + \phi} \exp \left[ -\frac{\phi}{\kappa + \phi} \tau \right] \\
v_{ss} &= 1 - \exp \left[ -\frac{\phi}{\kappa + \phi} \tau \right]
\end{align*}
\]
Concentration versus log time curves for reactant A, intermediate X and product P when full set of coupled rate equations are solved without any approximation. 

\( k_1 \gg k_2 \), \( k_2 \gg k_3 \) and \( k_1 = k_2 = 50 \). 
The concentration of intermediate X is very small and approximately constant throughout the time course of the experiment.

Concentration versus log time curves for reactant A, intermediate X, and product P when the rate equations are solved using the QSSA. Values used for the rate constants are the same as those used above. QSSA reproduces the concentration profiles well and is valid.

QSSA will hold when concentration of intermediate is small and constant. Hence the rate constants for getting rid of the intermediate \((k_1, k_2)\) must be much larger than that for intermediate generation \((k_1)\).

Concentration versus log time curves for reactant A, intermediate X and product P when the Coupled rate equations are solved using the quasi steady state approximation. The same values for the rate constants were adopted as above.

The QSSA is not good in predicting how the intermediate concentration varies with time, and so it does not apply under the condition where the concentration of intermediate will be high and the intermediate is long lived.