Complex Kinetics Explained

Lecture 1

Simple Kinetics

Assume the reaction

$$A \rightarrow B$$

The rate equation for the reaction will take the form

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

Solutions for simple rate equation

For the first order reaction this can be integrated and rearranged to get a solution for the concentration of a reactant over time – which is exponential.
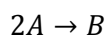
Integration

$$\int_{[A_0]}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

Solution (note that integral 1/x = ln x)

$$ln\frac{[A_0]}{[A]} = kt \qquad or \qquad [A] = [A_0]e^{-kt}$$

For a second order reaction

$$2A \rightarrow B$$
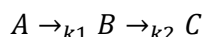
Rate equation

$$-\frac{d[A]}{dt} = k[A]^2$$

Integral

$$\int_{[A_0]}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Solution

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt \qquad or \qquad [A] = \frac{[A_0]}{1 + kt[A_0]}$$

Series (consecutive) reactions

Imagine the reaction

$$A \rightarrow_{k1} B \rightarrow_{k2} C$$

We can write down the rate equation for each component which results in a system of coupled differential equations:

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

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

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

Note the sign convention: the rate of reactant consumption (1) is negative, whilst for product formation (3) it is positive. By convention rates for intermediates (2) are positive.

The exact solution is possible here – one overall rate equation.

The exact solutions

From equation (1) we can solve and express the rate equation in terms of [A]:

$$[A] = [A_0]e^{-k_1 t} \quad (4)$$

This can be substituted into another differential equation that we made earlier (2) to make (5):

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

$$\frac{d[B]}{dt} = k_1[A_0]e^{-k_1 t} - k_2[B] \quad (5)$$

This can again be solved and expressed in terms of [B] (by multiplication by an integrating factor):

$$[B] = [A_0]\frac{k_1}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right] \quad (6)$$

This can be substituted into another differential equation that we made earlier (3) to make (7):

$$[C] = [A_0] - [A] - [B]$$

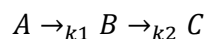$$[C] = [A_0] - [A_0]e^{-k_1 t} - [A_0]\frac{k_1}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right]$$

$$[C] = \frac{[A_0]}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right] \quad (7)$$

Even for this very simple composite scheme the equations are complex and non exponential

Limiting Cases

Let's look at our composite reaction again:

$$A \rightarrow_{k1} B \rightarrow_{k2} C$$

What happens when $k_1 \gg k_2$

The first reaction from A → B is really fast, whereas B → C is really slow.

What happens when $k_1 = k_2$

The first reaction from A → B is the same rate as B → C.

What happens when $k_1 \ll k_2$

The first reaction from A → B is really slow, whereas B → C is really fast.

Steady State Approximation (SSA)

The rate of reaction of reactive intermediates can be set equal to zero. This approximation dramatically simplifies the solution to composite reaction kinetics:

$$\frac{d}{dt}[I] = \cdots = 0$$

<u>Assumptions</u>

- The concentrations of all intermediates remain constant and small throughout the composite (complex) reaction (except right at the beginning and right at the end.
- The intermediate goes away as soon as it is made (highly reactive)

Remember that the SSA should be applied to reactive intermediates after the induction period.

What does expression for [C] reduce to under SSA?

Let's reconsider the reaction

$$A \rightarrow_{k1} B \rightarrow_{k2} C$$
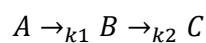
$$-\frac{d[A]}{dt} = k_1[A] \quad (1)$$

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

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

The application of the SSA assumes that any intermediates have no net rate of reaction:

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] = 0$$

Therefore:

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

Which we can substitute into equation (3)

$$\frac{d[C]}{dt} = k_2[B] \quad (3) \qquad [B] = \frac{k_1[A]}{k_2}$$

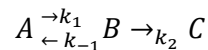$$\frac{d[C]}{dt} = k_2[B] = k_2\frac{k_1[A]}{k_2} = k_1[A] \quad (8)$$

And then substitute our first elementary solution (4) to get a final result:

$$[A] = [A_0]e^{-k_1 t} \quad (4)$$

$$\frac{d[C]}{dt} = k_1[A] = k_1[A_0]e^{-k_1 t} \quad (9)$$

Equilibrium Reactions

So far we have only looked at reactions which proceed all the way, but what about equilibrium reactions?

$$A \underset{\leftarrow k_{-1}}{\overset{\rightarrow k_1}{}} B \rightarrow_{k_2} C$$

It is a system of coupled differential equations and even more complex to solve

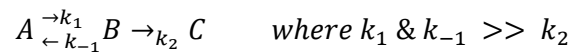$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] \quad (10)$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[C] \quad (11)$$

$$\frac{d[C]}{dt} = k_2[B] \quad (12)$$

But assume that both k_1 & k_{-1} >> k_2.

Then the reversible reaction is establishing a fast equilibrium and [B] changes slowly.

Quasi-equilibrium (fast equilibrium) approximation (QEA)

$$A \overset{\to k_1}{\underset{\leftarrow k_{-1}}{}} B \to_{k_2} C \qquad where \; k_1 \; \& \; k_{-1} \; >> \; k_2$$

Differential Equations

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] \quad (10)$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[C] \; (11)$$

$$\frac{d[C]}{dt} = k_2[B] \; (12)$$

Pre-equilibrium condition

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

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K_{eq}$$

And therefore:

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

To be added to: James 31/03/2014