

# Kinetics

Elementary Reactions  
 Reaction Order  
 Multi-step processes, Intermediates  
 Steady State Approximation  
 Photolysis in heme proteins  
 Photosynthesis

## Reaction Order

- The power to which a the concentration of a species is raised in the rate law is the reaction order. The overall order is the sum of all of the powers of all reactants.

Examples:

- $v = k[\text{NO}]^2[\text{O}_2]$  First order in  $\text{O}_2$ , Second order in NO, Third order overall.
  - $v = k[\text{A}]^{1/2}[\text{B}]^2$  Half order in A, Second order in B, 2 1/2 order overall.
- The order does not need to be an integer.

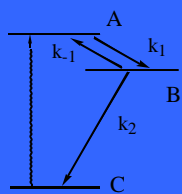
## Reaction order and molecularity

Reaction order is an empirical quantity.  
 Molecularity refers to an elementary reaction as a step in a reaction mechanism.  
 The rate law of an *elementary step* can be deduced directly from the reaction.  
 Unimolecular reactions are first order.  
 $\text{A} \rightarrow \text{Products} \quad d[\text{A}]/dt = -k[\text{A}]$   
 Bimolecular reactions are second order.  
 $\text{A} + \text{B} \rightarrow \text{Products} \quad d[\text{A}]/dt = -k[\text{A}][\text{B}]$

## An example: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

The formation of nitric oxide is a termolecular reaction, i.e. three molecules must collide in order for the products to be formed. In this example the reaction is also the elementary step and so the rate law is  $v = k[\text{NO}]^2[\text{O}_2]$  as stated earlier. In this case the reaction is third order *because of the fact that three molecules must combine simultaneously*. However, the reaction stoichiometry may not always indicate the molecularity of the reaction.

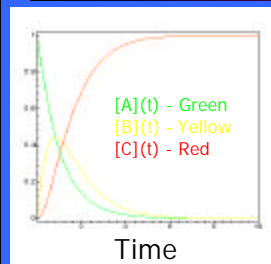
## Sequential first-order reactions Consecutive elementary reactions



- $\text{A} \leftrightarrow \text{B} \rightarrow \text{C}$  rate equations are:
- $d[\text{A}]/dt = -k_1[\text{A}] + k_{-1}[\text{B}]$
- $d[\text{B}]/dt = k_1[\text{A}] - (k_2 + k_{-1})[\text{B}]$
- $d[\text{C}]/dt = k_2[\text{B}]$
- A and B are in equilibrium
- Either  $k_1$  or  $k_2$  can be the rate limiting step.

We will not explicitly solve the system of equations here.

## Populations as a function of time



- The population as a function of time is given by the solutions to the sequential first order reactions.
- The case shown is intermediate with  $k_2 = 1.5k_1$ .
- The population of B grows and reaches a maximum and then decays.

## Rate determining step

- If  $k_2 \gg k_1$  then the first ( $A \rightarrow B$ ) step becomes the rate-limiting step.
- If the  $A \rightarrow B$  step is rate limiting then little or no B will be observed even though it is formed on the reaction path.
- If  $k_1 \gg k_2$  then the second ( $B \rightarrow C$ ) step becomes the rate limiting step.
- If the  $B \rightarrow C$  step is rate limiting then there will be a significant build-up of the intermediate state B.

## Steady-state approximation

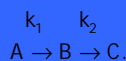
- Equations representing kinetic networks of more than three states are not soluble analytically.
- One means of pushing the techniques as far as possible using analytical solutions is to set the derivatives of intermediates equal to zero:

$$d[\text{Intermediate}]/dt = 0$$

- The build-up of intermediate B shown in the figure (two slides back) implies that the steady state approximation does not work for the system shown there.

## Application of the steady-state approximation

- The steady state approximation can be applied to the consecutive reaction scheme



if the concentration of B is fairly constant.

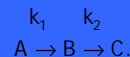
- The result of setting  $d[B]/dt = 0$  is that we find at once that

$$k_1[A] - k_2[B] = 0$$

and  $d[C]/dt = k_1[A]$ ,  $[C] = (1 - \exp\{-k_1 t\})$

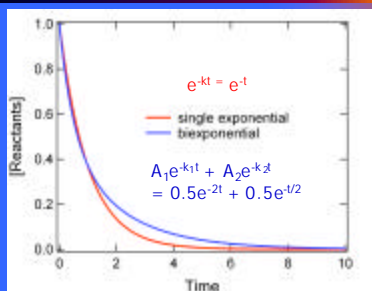
## Biexponential kinetics result when the steady-state approximation fails

- We cannot apply the steady state approximation if the concentration of B changes significantly during the process

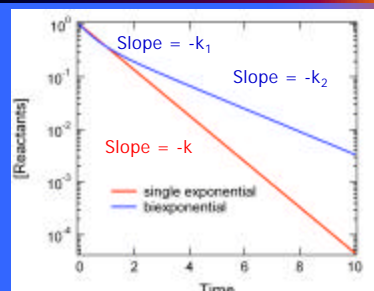


- In this case we must solve the rate equations
- In general, for N processes the result will be kinetics with N exponential time constants. Here:  $[A](t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t}$

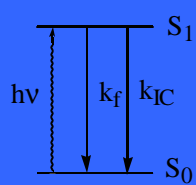
## Distinguishing single and biexponential kinetics



## Distinguishing single and biexponential kinetics on a log plot



## Competing or parallel processes



Photoexcitation  
followed by return  
to the S<sub>0</sub> ground state.

- Decay of the singlet S<sub>1</sub> state can occur either radiatively by fluorescence (k<sub>f</sub>) or by internal conversion (k<sub>IC</sub>).
- $d[S_1]/dt = -(k_f + k_{IC})[S_1]$
- The overall decay rate constant is the sum of the rate constants.

The fluorescence quantum yield is

$$\Phi = \frac{k_f}{k_f + k_{IC}}$$