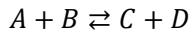


# BIOE 198MI Biomedical Data Analysis. Spring Semester 2018.

## Lab 5: Modelling Chemical Equilibria

### Problem Statement.

You are in charge of engineering of a large scale reaction modeled by the following equation:



The forward reaction's kinetics are first-order with respect to the concentration of A, [A], and the reverse reaction is first-order with respect to the concentration of C, [C].

The forward equilibrium constant  $k_f = 0.2 \text{ s}^{-1}$  and, the reverse equilibrium constant  $k_r = 2 \text{ s}^{-1}$ .

How can we model this reaction and determine different methods to control the results of the reaction?

### Definition of “order” for equilibrium kinetics:

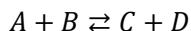
$$r_f = k_f[A]^m[B]^n$$

For a given reaction with rate and equilibrium constant , the *order* of the reaction is defined at the sum of the powers,  $m + n$ .

Equilibrium constants are useful to describe reaction kinetics because the other values in the reaction rate equation ( $r_f$ , [A], [B]) are functions of time, i.e. time variant.

### Problem Walkthrough

%% Modeling a First Order Reaction



The forward ( $r_f$ ) and reverse ( $r_r$ ) reaction rates are described by the following equations:

$$r_f = \begin{cases} k_f[A]^1[B]^0, & [A] > 0 \text{ and } [B] > 0 \\ 0, & \text{else} \end{cases} \quad \text{EQN (i)}$$

$$r_r = \begin{cases} k_r[C]^1[D]^0, & [C] > 0 \text{ and } [D] > 0 \\ 0, & \text{else} \end{cases} \quad \text{EQN (ii)}$$

Where  $r_f$  and  $r_r$  are reaction rates with units of  $(M \text{ changed})(\text{s})^{-1}$  and  $k_f$  and  $k_r$  are equilibrium constants with units of  $(\text{s})^{-1}$ . (Remember  $M = \text{mol/L}$ ).

Note that  $r_f$  and  $r_r$  are only positive when there are positive amounts of the respective reactants needed for the reaction to proceed.

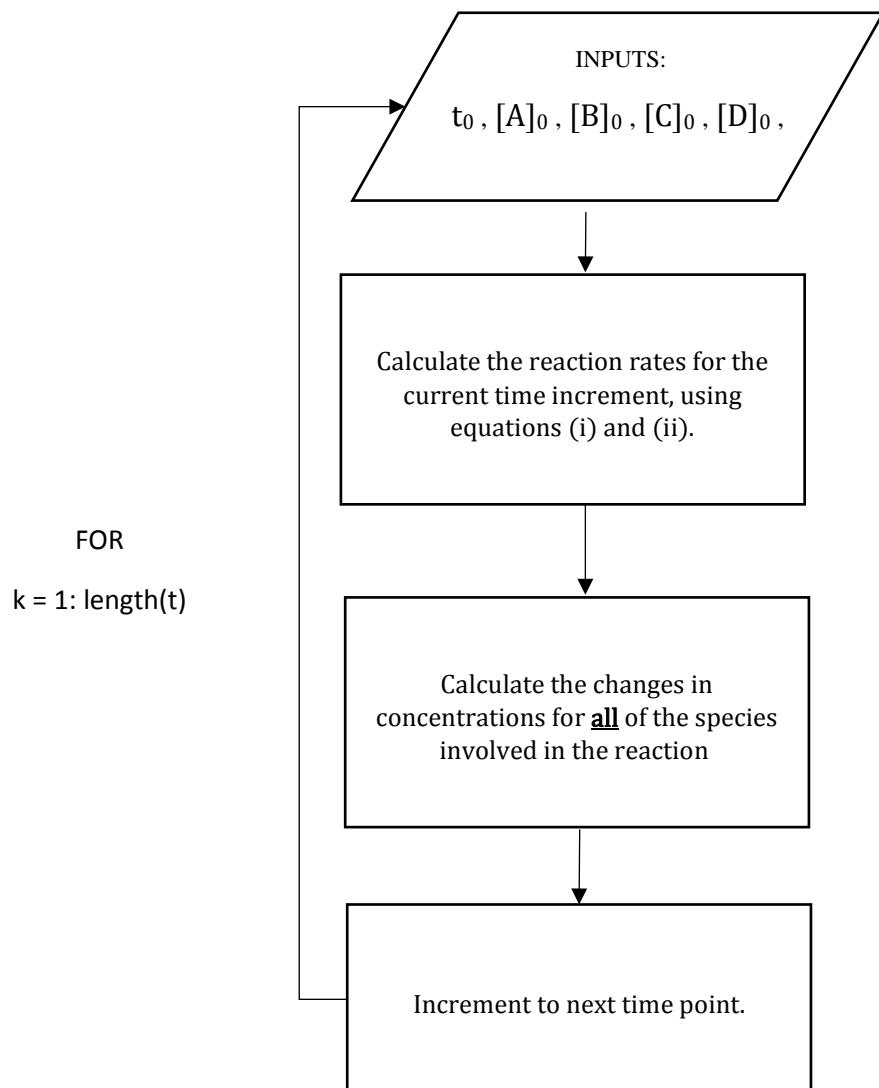
Given:  $[A]_0 = 10 M$ ,  $[B]_0 = 20 M$ ,  $[C]_0 = 5 M$ ,  $[D]_0 = 15 M$   
 $k_f = 0.2 \text{ s}^{-1}$ ,  $k_r = 2 \text{ s}^{-1}$ .

Remember, only  $k_f$  and  $k_r$  are time invariant. In order to model this process, think about  $r_f$ ,  $r_r$ , [A], [B], [C], and [D] as functions of time.

You can visualize those variables as below:

$t_0$	$t_1$	...	$t_n$
$r_{f,0}$	$r_{f,1}$	...	$r_{f,n}$
$r_{r,0}$	$r_{r,1}$	...	$r_{r,n}$
$[A]_0$	$[A]_1$	...	$[A]_n$
$[B]_0$	$[B]_1$	...	$[B]_n$
$[C]_0$	$[C]_1$	...	$[C]_n$
$[D]_0$	$[D]_1$	...	$[D]_n$

So to model the reaction over a given time period, follow these steps:



Let's walk through this for just the forwards reaction.  
This means for now we can set  $r_f = 0$ .

Step 1. Calculate the reaction rates for the current time increment

$$r_f(t_0) = \begin{cases} k_f([A](t_0))^1([B](t_0))^0, & [A](t_0) > 0 \text{ and } [B](t_0) > 0 \\ 0 & \text{else} \end{cases}$$

Step 2. Calculate the changes in concentrations for all of the species involved in the reaction

$$\begin{aligned} [A](t_1) &= [A]_0 - \Delta[A]_{\text{consumed}} + \Delta[A]_{\text{produced}} \\ &= [A](t_0) - r_f(t_0) \cdot \Delta t + 0 \\ [B](t_1) &= [B]_0 - \Delta[B]_{\text{consumed}} + \Delta[B]_{\text{produced}} \\ &= [B](t_0) - r_f(t_0) \cdot \Delta t + 0 \\ [C](t_1) &= [C]_0 - \Delta[C]_{\text{consumed}} + \Delta[C]_{\text{produced}} \\ &= [C](t_0) - 0 + r_f(t_0) \cdot \Delta t \\ [D](t_1) &= [D]_0 - \Delta[D]_{\text{consumed}} + \Delta[D]_{\text{produced}} \\ &= [D](t_0) - 0 + r_f(t_0) \cdot \Delta t \end{aligned}$$

Step 3. Repeat steps 1-2 for all time increments.

A general equation for the reaction rate at each time-point ( $t_n$ ):

$$r_f(t_n) = \begin{cases} k_f([A](t_n))^1([B](t_n))^0, & [A](t_n) > 0 \text{ and } [B](t_n) > 0 \\ 0 & \text{else} \end{cases}$$

General equations calculating changes in concentration for each timepoint ( $t_n$ ) can be calculated using the values for the previous timepoint ( $t_{n-1}$ ).

$$\begin{aligned} [A](t_n) &= [A]_{n-1} - \Delta[A]_{\text{consumed}} + \Delta[A]_{\text{produced}} \\ &= [A](t_{n-1}) - r_f(t_{n-1}) \cdot \Delta t + 0 \\ [B](t_n) &= [B]_{n-1} - \Delta[B]_{\text{consumed}} + \Delta[B]_{\text{produced}} \\ &= [B](t_{n-1}) - r_f(t_{n-1}) \cdot \Delta t + 0 \\ [C](t_n) &= [C]_{n-1} - \Delta[C]_{\text{consumed}} + \Delta[C]_{\text{produced}} \\ &= [C](t_{n-1}) - 0 + r_f(t_{n-1}) \cdot \Delta t \\ [D](t_n) &= [D]_{n-1} - \Delta[D]_{\text{consumed}} + \Delta[D]_{\text{produced}} \\ &= [D](t_{n-1}) - 0 + r_f(t_{n-1}) \cdot \Delta t \end{aligned}$$

This should line up with the matrix representation of our variables that we had previously.

$t_0$	$t_1$	...	$t_n$
$r_{f,0}$	$r_{f,1}$	...	$r_{f,n}$
$r_{r,0}$	$r_{r,1}$	...	$r_{r,n}$
$[A]_0$	$[A]_1$	...	$[A]_n$
$[B]_0$	$[B]_1$	...	$[B]_n$
$[C]_0$	$[C]_1$	...	$[C]_n$
$[D]_0$	$[D]_1$	...	$[D]_n$

1. Write a set of equations to calculate the changes in concentration for A, B, C, and D, this time adding in the reverse reaction.

Use equations (i) and (ii) as starting points.

Program a simulation of the whole reaction (both the forward and reverse reactions) for 30 seconds and plot  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  as functions of time. You will need to select a time increment,  $\Delta t$ . As part of your answer, *justify your choice for  $\Delta t$* .

Things to watch out for:

- Don't forget to make sure the reaction rates are set to zero if there are no reactants to drive the reaction. What function would let you do this?
- What happens if your simulation calculates a negative value for one of the concentrations? Is that meaningful?

`%% Looking at distributions of initial conditions`

Now instead of constant values we can use distributions for initial conditions.

$$\begin{aligned}[A]_0 &\sim \text{Normal}(\mu = 10 \text{ M}, \sigma = 2.5 \text{ M}) \\ [B]_0 &= 20 \text{ M}, [C]_0 = 5 \text{ M}, [D]_0 = 15 \text{ M}\end{aligned}$$

Run *StudentVer2.m* (lines 98-116).

Use plotting functions to see what  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  as functions of time looked like in the different simulations.

Modify the code to run a simulation with distributions for all of the initial conditions.

$$\begin{aligned}[A]_0 &\sim \text{Normal}(\mu = 10 \text{ M}, \sigma = 2.5 \text{ M}) \\ [B]_0 &\sim \text{Normal}(\mu = 20 \text{ M}, \sigma = 2.5 \text{ M}) \\ [C]_0 &\sim \text{Normal}(\mu = 5 \text{ M}, \sigma = 2.5 \text{ M}) \\ [D]_0 &\sim \text{Normal}(\mu = 15 \text{ M}, \sigma = 2.5 \text{ M})\end{aligned}$$

How can we explore the relationships between the initial conditions and final conditions for A, B, C, and D using functions like histogram and scatter?

**Assignment:**Reaction 1:  $A + B \rightleftharpoons C$ Reaction 2:  $C + D \rightleftharpoons E + F$ 

$$r_{f,1} = k_{f,1}[A]^1[B]^1$$

$$r_{r,1} = k_{r,1}[C]^1$$

$$r_{f,2} = k_{f,2}[C]^1[D]^0$$

$$r_{r,2} = k_{r,2}[E]^1[F]^1$$

Given:

$$[C]_{0,max} = 10 M, [D]_{0,max} = 20 M, [E]_{0,max} = 5 M, [F]_{0,max} = 15 M$$

$$k_{f,1} = 0.2 \text{ M}^{-1}\text{s}^{-1}, k_{r,1} = 2 \text{ s}^{-1}$$

$$k_{f,2} = 2 \text{ M}^{-1}\text{s}^{-1}, k_{r,2} = 0.5 \text{ s}^{-1}$$

Deliverables:

1. Provide the change in concentration equations for C.
2. What is the relationship between A, B, E, and F?
3. What conditions will maximize the product C?