

## *Reacting System Examples*

Here are six examples of the chemical systems. The goal of this handout is to show you how to formulate a model of a chemical system, but some of the examples include solutions using methods you will learn later this week or later in the term, so that you get to see what happens in the system and build your intuition about system behavior.

The first three examples are typical examples based on the methods you are expected to learn for the course. They include solutions, although the solutions are sometimes based on methods you will learn later in the course.

Example 1: Sequential reactions. An example based on the chemical process industry. p. 1

Example 2: Respiration in a submersible vessel. p. 6

Example 3: Waste treatment pond. p. 7

The next two examples are included to demonstrate the wide variety of applications of these methods, although they are not typical examples for the material in 22. Models are developed by not solved.

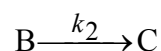
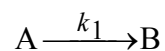
Example 4: Blood alcohol. A model for blood alcohol in the human body after consumption of alcoholic beverages. p. 8

Example 5: Oxygen sag curve. Oxygen level in a stream or river downstream of a pollution source. p. 11

### **Example 1. Sequential reactions.**

*Background:* In the chemical process industry, it is often the case that one or more reactants are converted to one or more desired chemicals under conditions such that the desired chemicals can also react further to form undesired byproducts. One example is in the cracking of crude oil, where high molecular weight non-volatile liquid reactants are converted to intermediate molecular weight volatile liquids suitable for gasoline, but these intermediate molecular weight liquids also react to form low molecular weight gases. Such gases, although sold, are worth less than the intermediate molecular weight volatile liquids. So the goal is the form as much as possible of the volatile liquids, while avoiding allowing the liquids to react further and produce gasses.

The simplest representation of a system with the general features described above involves two reactions:



B is the desired product (e.g. volatile liquids), whereas C is not desired.

*Problem Statement:*

Given the reaction described above, you wish to find the following quantities:

- Maximum value of B that can be realized in well-mixed reactors operated in either batch or steady-state continuous mode.
- The time or "residence time" at which this occurs, in both batch and continuous mode.
- The reactor volume required to produce 100 moles B/hr, again in batch and continuous mode.

The following information is given:

$$C_{A,0} = 1 \text{ mole/L}; \quad C_{B,0} = C_{C,0} = 0$$

$$k_1 = 3 \text{ hr}^{-1}, \quad k_2 = 0.7 \text{ hr}^{-1}$$

Reaction time for the continuous reactor = mean liquid residence time =  $V/Q = \theta$ , where  $V$  = system volume,  $Q$  = volumetric flow rate.

Assume that the reactors are well-mixed and have constant volume, that the reactions occur in the liquid phase, and (for the continuous reactor) that the input and output liquid flow rates are the same.

*Formulation of the system model.*

- a. Write the rate laws.

Based on the indicated mechanism, we can write the rate laws for each chemical species:

$$r_A = -k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

- b. Write appropriate material balance equations.

*Batch case*

Material balance equations for each of the three reacting species:

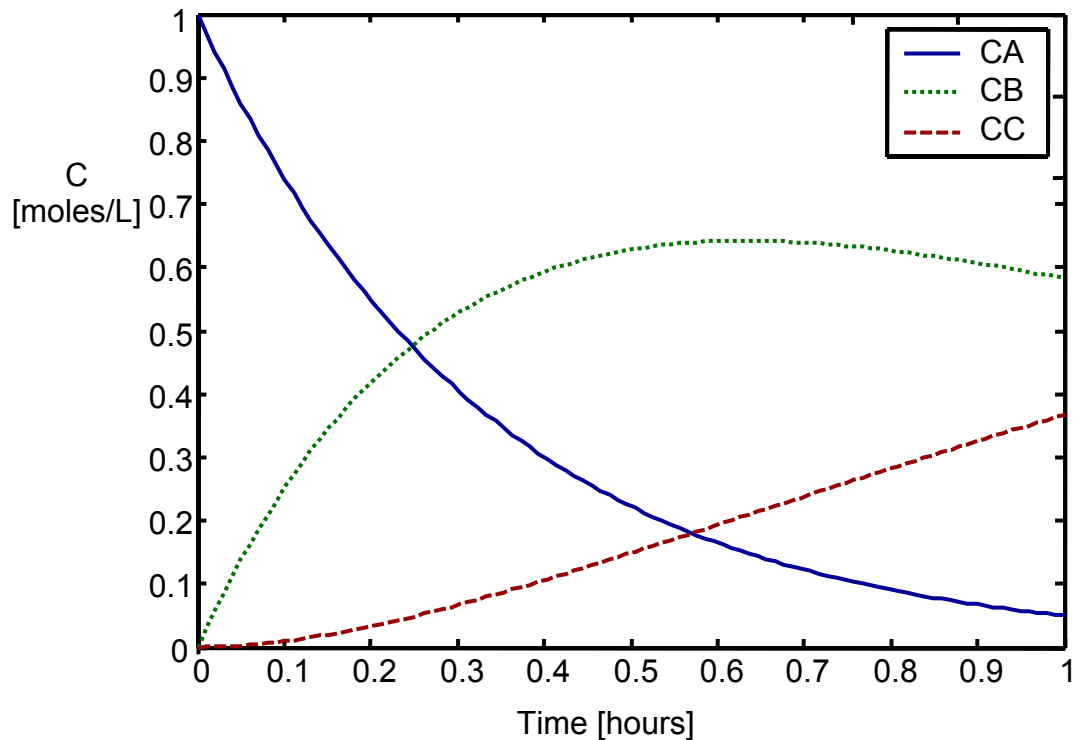
$$\frac{dC_A}{dt} = r_A = -k_1 C_A$$

$$\frac{dC_B}{dt} = r_B = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = r_C = k_2 C_B$$

This is the system model for the batch case: three simultaneous first-order linear ordinary differential equations.

We'll come back to model formulation for the CSTR case after looking at a solution to the above equations. We can solve them by various means, which we will study later in the class—one good choice, and one that you will learn soon, would be a numerical simulation using MATLAB. It is also possible to use the Laplace transform (as detailed in the appendix, although you aren't expected to learn this until later in the term). The results of the solution are shown below.



At 0.63 hours, the concentration of B reaches a maximum value of 0.64 moles/liter. This *volumetric productivity* of this reactor is

$$\frac{0.64 \frac{\text{moles}}{\text{L}}}{0.63 \text{ hr}} = 1.015 \frac{\text{moles}}{\text{L hr}}$$

If we want to produce 100 moles/hr, we need a reactor of volume

$$V = \frac{100 \frac{\text{moles}}{\text{hr}}}{1.015 \frac{\text{moles}}{\text{L hr}}} = 99 \text{ L}$$

*Continuous case*

For a continuous reactor, the material balance equation is of the form (for A)

$$\frac{dC_A}{dt} = \frac{Q}{V}(C_{A,in} - C_{A,out}) + r_A$$

We are interested only in the steady state response, so set the derivative to zero.

$$C_{A,in} - C_A + \theta r_A = 0$$

where  $\theta = V/Q$ , and  $C_{out} = C$  for a well-mixed reactor. We write an equation for each species, and substitute the rate laws to obtain three algebraic equations:

$$\begin{aligned} C_{A,in} - C_A - \theta k_1 C_A &= 0 \\ C_{B,in} - C_B + \theta(k_1 C_A - k_2 C_B) &= 0 \\ C_{C,in} - C_C + \theta k_2 C_B &= 0 \end{aligned}$$

Only A is put into the reactor, at a concentration  $C_{A,in} = C_{A,o}$ , and  $C_{B,in} = C_{C,in} = 0$ . Solving the equations,

$$\begin{aligned} C_A &= \frac{C_{A,o}}{1 + \theta k_1} \\ C_B &= \frac{\theta k_1 C_A}{1 + \theta k_2} = \frac{\theta k_1 C_{A,o}}{(1 + \theta k_2)(1 + \theta k_1)} \\ C_C &= \frac{\theta^2 k_2 k_1 C_{A,o}}{(1 + \theta k_2)(1 + \theta k_1)} \end{aligned}$$

Again,  $C_A + C_B + C_C = C_{A,o}$ , as they should. In this problem, the independent variable is the residence time,  $\theta = V/Q$ . We can use Matlab to plot the steady-state concentrations as a function of  $\theta$ . This is not using Matlab to solve differential equations of anything of that sort—just as a plotting utility now that we know the solution.

```
% reacting systems example 2
% ENGS 22
% Charlie Sullivan

CA0 = 1;      % Moles/L
k1 = 3;      % 1/hr
k2 = 0.7;    % 1/hr

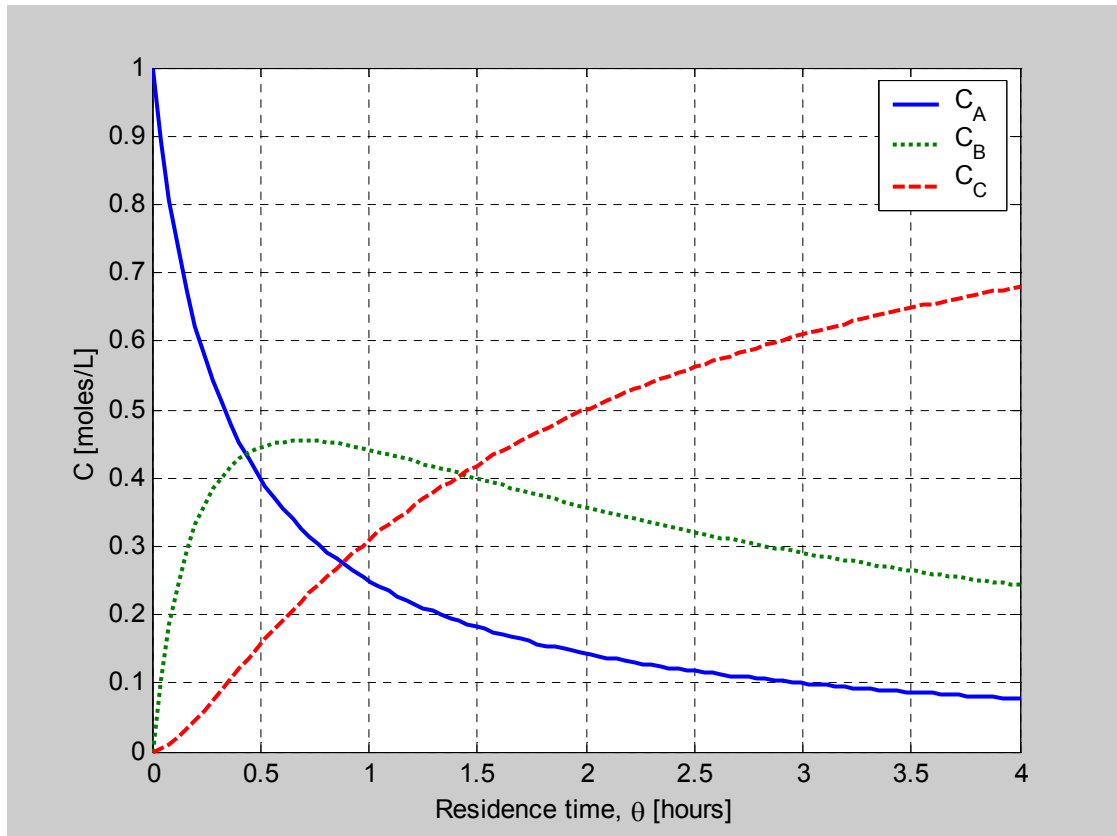
theta = linspace(0,4);
CA = CA0 ./ (1 + k1*theta);
CB = theta.*k1.*CA ./ (1 + theta*k2);
CC = theta.*k2.*CB;

plot(theta,CA, theta,CB, ':', theta,CC, '--'), grid
xlabel('Residence time, \theta [hours]'), ylabel('C [moles/L]')
legend('C_A', 'C_B', 'C_C')
```

The maximum concentration of  $B$ , about 0.455 moles/liter, occurs with a residence time of 0.69 hr. The volumetric productivity is

$$\frac{0.45 \frac{\text{moles}}{\text{L}}}{0.68 \text{ hr}} = 0.67 \frac{\text{moles}}{\text{L hr}}$$

To produce 100 moles/hr with this process, we would need a reactor volume of about 150 L. For this particular example, the batch reactor is superior to the continuous reactor.



Intuitively, the superiority of the batch reactor makes sense. During the batch reaction cycle,  $C_A$  is higher than its final value (increasing the rate of conversion of  $A$  to  $B$ ) and  $C_B$  is lower than its final value (decreasing the rate of conversion of  $B$  to  $C$ ). By contrast, in the continuous reactor,  $C_A$  and  $C_B$  are at their effluent values for all time once the system is at steady state.

Equivalent performance to the batch reactor may be realized in a continuous plug flow reactor – thus providing the advantage of constant operation, with the better performance of the batch reactor.

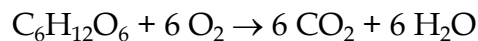
**Example 2: Respiration in a submersible vessel***Problem statement*

Consider a submersible vessel designed for underwater exploration. How long can two persons be underwater, supported by the air initially present in the vessel?

Here's what we know:

Volume of the vessel =  $20 \text{ m}^3$

Stoichiometry of respiration:



Properties of air at atmospheric pressure,

$$C_{\text{O}_2} = 7 \times 10^{-3} \text{ moles/liter}$$

$$C_{\text{CO}_2} = 1 \times 10^{-5} \text{ moles/liter}$$

Rate of metabolism, resting = 1 mole  $\text{O}_2$ /hr per person

Toxicity threshold,

$$C_{\text{CO}_2} \geq 1.8 \times 10^{-3} \text{ moles/liter is toxic.}$$

Minimum oxygen to support human life,

$$C_{\text{O}_2} \geq 4 \times 10^{-3} \text{ moles/liter required to support human life.}$$

*Solution*

## Rate law

The rate of  $\text{O}_2$  consumption is fixed at 2 mole/hr (for 2 people), independent of concentration. The rate law is simply

$$r_{\text{O}_2} = -\frac{2 \text{ moles O}_2/\text{hr}}{20 \text{ m}^3} = -0.1 \frac{\text{moles O}_2}{\text{m}^3 \text{ hr}} = -0.0001 \frac{\text{moles O}_2}{\text{L hr}}$$

The rate of  $\text{CO}_2$  production is the same as the rate of  $\text{O}_2$  consumption, since 1 mole of  $\text{CO}_2$  is produced for each mole of  $\text{O}_2$  consumed.

## Material balance

The vessel may be modeled as a constant volume, well-mixed batch reactor with one reaction. The material balance equations are

$$\frac{dC_{O_2}}{dt} = r_{O_2}$$

$$\frac{dC_{CO_2}}{dt} = -r_{O_2}$$

This completes the formulation of this problem. At this point in the course, we generally cannot solve systems, except by using numerical methods. However, in this case we can, so it is useful to go ahead and solve it.

Because these just have constants on the right hand side, we don't need any high-powered solution methods, and can just integrate them to get:

$$C_{O_2,final} - C_{O_2,initial} = r_{O_2}t$$

$$C_{CO_2,final} - C_{CO_2,initial} = -r_{O_2}t$$

We substitute the toxicity thresholds for  $C_{final}$  and the nominal atmospheric concentrations for  $C_{initial}$ , and solve for  $t$ .

$$t_{O_2} = \frac{C_{O_2,final} - C_{O_2,initial}}{r_{O_2}} = \frac{4 \times 10^{-3} \frac{\text{moles}}{\text{L}} - 7 \times 10^{-3} \frac{\text{moles}}{\text{L}}}{-0.0001 \frac{\text{moles}}{\text{L hr}}} = 30 \text{ hr}$$

$$t_{CO_2} = \frac{C_{CO_2,final} - C_{CO_2,initial}}{-r_{O_2}} = \frac{1.8 \times 10^{-3} \frac{\text{moles}}{\text{L}} - 0.01 \times 10^{-3} \frac{\text{moles}}{\text{L}}}{0.0001 \frac{\text{moles}}{\text{L hr}}} = 17.9 \text{ hr}$$

The  $CO_2$  buildup is the ultimate constraint. The time limit is just under 18 hr. The divers will suffer hypercapnia (too much  $CO_2$ ) before they become hypoxic (too little  $O_2$ ).

### Example 3: Waste treatment pond

Continuous feed, constant volume, well-mixed reactor,  $C_{out} = C_A = C$

Material balance:

$$\frac{dC}{dt} = -\frac{Q}{V}C + r^f + \frac{Q}{V}C_{in}$$

Reaction mechanism:  $A \rightarrow B$  with rate constant  $k$

$$r^f = -kC$$

Combine material balance with rate law,

$$\frac{dC}{dt} = -\frac{Q}{V}C - kC + \frac{Q}{V}C_{in}$$

Steady state solution: Steady state implies derivatives are equal to zero. Setting the derivative equal to zero, we find:

$$C_{ss} = \frac{Q/V}{(Q/V + k)} C_{in} = \frac{1}{(1 + kV/Q)} C_{in}$$

The concentration of pollutant leaving the pond can be reduced by increasing the volume or decreasing the flow rate (stuff stays around longer before being washed out), or designing a better reaction (higher  $k$ ).

For unsteady (transient) situations, we can use the differential equations above in a computer simulation, or solve them analytically, as we will learn later in the course.

(The result comes out as

$$C(t) = C(0)\exp\left(-\frac{t}{\tau}\right) + \frac{C_{in}}{(1 + kV/Q)}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right)$$

$$\tau = \frac{1}{Q/V + k} = \frac{V/Q}{(1 + kV/Q)}$$

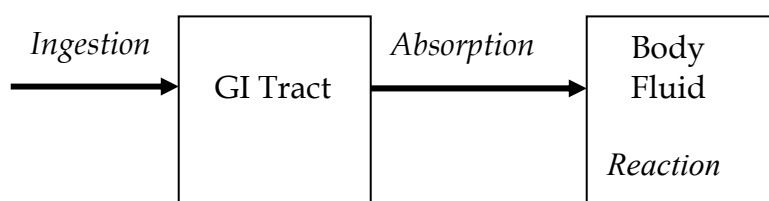
$V/Q$  is the time constant in the absence of the reaction, also known as the *residence time*, or average time that a molecule of A is in the pond. That time is shortened by the reaction, since the reaction provides an alternate pathway to simply being washed out by the flow.)

#### Example 4. Blood alcohol.

*Background.* Quantitative modeling of biological systems is of interest both to test our understanding and to predict behavior of such systems. Understanding the dynamic behavior of blood alcohol levels, the subject of this example, is of obvious interest in terms of informing behavior and related guidelines aimed at responsible use of alcohol.

The following simplified model for blood alcohol absorption and reaction is based on that presented by Fogler (Elements of Chemical Reaction Engineering, 3<sup>rd</sup> ed., Prentice Hall, 1999.). This two-compartment model (Fig. 1) features ingested alcohol entering the gastrointestinal (GI) tract, transported across the stomach wall from the GI to the body fluid (BF), and then reaction in the body fluid. A more elaborate model would probably consider transport from the body fluid into the urine and subsequent excretion but these features are not examined here.

Fig. 1. Schematic representation of blood alcohol model (modified from Fogler)



The rate of transport ( $r_{\text{transport}}$ , g alcohol/(L GI volume·hr)) is a function of the alcohol concentrations in the GI and BF,  $C_{A,\text{GI}}$  and  $C_{A,\text{BF}}$  respectively:

$$r_{\text{transport}} = k_{\text{trans}}(C_{A,\text{GI}} - C_{A,\text{BF}})$$

where

$$k_{\text{trans}} = \text{transport rate constant } 10 \text{ hr}^{-1}$$

The rate of reaction of alcohol is limited by the concentration of a required co-enzyme rather than by the concentration of alcohol. Thus the rate can be said to be zero<sup>th</sup> order (independent of concentration) with respect to alcohol as long as the concentration of alcohol in the body fluid is greater than 0. The rate of ethanol being depleted by reaction is 0.192 g alcohol/(h·L body fluid). Thus we have

$$r_{\text{reaction}} = 0.192$$

the sign of  $r$  depends on whether we are considering the GI (negative) or the BF (positive).  
Additional information:

For  $m$  = body mass (kg)

$$\text{Body fluid volume, } V_{\text{BF}} = (0.5 \text{ L/kg}) \cdot m$$

$$\text{Gastrointestinal tract fluid volume, } V_{\text{GI}} = (0.02 \text{ L/kg}) \cdot m$$

Amount of ethanol in a tall martini: 40 g

Legal limits on blood alcohol, in terms of  $C_{E,\text{BF}}$  (g ethanol/L body fluid)

United States: 1 g/L

Sweden: 0.5 g/L

Following initial ingestion of alcohol, the GI fluid and body fluid may be modeled as well-mixed batch reactors. Each of these can be assumed to have constant volume over time, although their volumes differ from each other.

We would like to know what time period is required after consuming two tall martinis before the blood alcohol level will be below the legal limit for the following cases:

U.S. limit, 50 kg and 100 kg person

Swedish limit, 50 kg and 100 kg person

*Formulation of the system model*

- a. Rate laws (given above).
- b. Material balances (this time for the same component in two different locations).

For the GI, assuming that we have calculated an initial value of  $C_{A,GI}$  following ingestion of alcohol:

$$\frac{dC_{A,GI}}{dt} = \mathbf{r}_{trans} = -k_{trans}(C_{A,GI} - C_{A,BF}) \quad (\text{units: g/(L GI fluid}\cdot\text{hr)}) \quad [1]$$

For the BF:

$$V_{BF} \frac{dC_{A,BF}}{dt} = V_{GI} k_{trans} C_{E,GI} + V_{BF} \mathbf{r}_{reaction} \quad (\text{units: g/hr}) \quad [2]$$

Dividing by  $V_{BF}$  we obtain

$$\frac{dC_{A,BF}}{dt} = 0.04 k_{trans} C_{A,GI} + \mathbf{r}_{reaction} \quad (\text{units: g/(L body fluid}\cdot\text{hr)}) \quad [3]$$

Equations [1] and [3] constitute the system model.

**Example 5. Oxygen sag curve.**

*Background.* Analysis of reacting systems arises can be applied to the environment with respect to the dynamic behavior of both engineered systems to consume a pollutant and also the behavior of the environment itself. This example concerns the derivation of a classic equation arising in the latter context, the *Streeter-Phelps* equation, which can be used to predict the dissolved concentration downstream of a point of pollutant discharge. Typically, we want to find the minimum oxygen concentration that will result, and where this will occur. This minimum can be compared to threshold values to determine if a proposed discharge is acceptable.

*Model formulation.* The concentration of dissolved oxygen  $C_{O_2}$  is a critical determinant of water quality. When wastewater (either municipal or industrial) containing organic matter is discharged into a stream,  $C_{O_2}$  is determined by the balance between two competing processes:

- 1) oxygen depletion (“deaeration”) due to consumption of organic matter by aerobic organisms (primary microorganisms),
- 2) oxygen addition (“reaeration”) due to mass transfer from the air above the river.

Consumption of organic matter commonly modeled as first order with respect to the concentration of organic matter,  $C_{OM}$ . Thus

$$r_{OM} = -k_1 C_{OM}$$

It is standard to express  $C_{OM}$  in units of mg  $O_2$  necessary for organic matter oxidation per liter. With this convention, the consumption of organic matter is also equal to the rate of deaeration.

Reaeration is commonly modeled as being proportional to the difference between the concentration of dissolved oxygen in equilibrium with air and the actual concentration of dissolved oxygen in the river. The concentration of oxygen in equilibrium with air is a physical property independent of the system state corresponding to the solubility of oxygen, denoted  $C_{O_2, sat}$ . Thus

$$r_{reaeration} = k_2(C_{O_2, sat} - C_{O_2})$$

Formulate a system model for the concentration of dissolved oxygen in the stream, modeling the stream as a plug flow reactor.

*Problem formulation.*

As in the previous example, the problem statement includes the rate laws, so we proceed directly to the material balance. Using a frame of reference moving at the velocity of the river, we can write material balance equations for both organic matter and oxygen:

$$\text{Organic matter: } \frac{dC_{OM}}{dt} = r_{OM} = -k_1 C_{OM}$$

$$\text{Oxygen: } \frac{dC_{O_2}}{dt} = r_{OM} + r_{reaeration} = -k_1 C_{OM} + k_2(C_{O_2, sat} - C_{O_2})$$

**Appendix:** Solution to the first example problem using Laplace transforms, for reference. Laplace transformers will be introduced later in the course. You aren't expected to be able to follow this now, but if, after you learn Laplace transforms, you want to see how they can be applied to a chemical example, here you are. (It is rare that they can be applied, since usually chemical systems are nonlinear, but these equations are linear.)

After the Laplace transform is applied to the system model, it becomes:

$$\begin{aligned}(s+k_1)C_A(s) &= C_{A,o} \\ -k_1C_A(s) + (s+k_2)C_B(s) &= C_{B,o} \\ -k_2C_B(s) + sC_C(s) &= C_{C,o}\end{aligned}$$

We can just solve these algebraic equations top to bottom:

$$\begin{aligned}C_A(s) &= \frac{C_{A,o}}{s+k_1} \\ C_B(s) &= \frac{C_{B,o}}{s+k_2} + \frac{k_1C_{A,o}}{(s+k_1)(s+k_2)} = \frac{k_1C_{A,o}}{(s+k_1)(s+k_2)} \\ C_C(s) &= \frac{C_{C,o}}{s} + \frac{k_2C_{B,o}}{s(s+k_2)} + \frac{k_1k_2C_{A,o}}{s(s+k_1)(s+k_2)} = \frac{k_1k_2C_{A,o}}{s(s+k_1)(s+k_2)}\end{aligned}$$

where we have used the fact that the initial concentrations of B and C are zero. Inverting the transforms by the usual means leads to

$$\begin{aligned}C_A(t) &= C_{A,o} \exp(-k_1t) \\ C_B(t) &= \frac{k_1}{k_2-k_1} C_{A,o} \exp(-k_1t) - \frac{k_1}{k_2-k_1} C_{A,o} \exp(-k_2t) \\ C_C(t) &= C_{A,o} - \frac{k_2}{k_2-k_1} C_{A,o} \exp(-k_1t) + \frac{k_1}{k_2-k_1} C_{A,o} \exp(-k_2t)\end{aligned}$$

Note that  $C_A + C_B + C_C = C_{A,o}$ , indicating that the total number of moles of the reacting species in the batch reactor must be the same for all time.

The following Matlab code will plot the results

```
% reacting systems example 1
% ENGS 22, Charlie Sullivan

CA0 = 1;      % Moles/L
k1 = 3;      % 1/hr
k2 = 0.7;    % 1/hr

t = linspace(0,5);
CA = CA0 * exp(-k1*t);
CB = k1*CA0/(k2-k1) * (exp(-k1*t) - exp(-k2*t));
CC = CA0 - CA - CB;

plot( t, CA, t,CB,':', t,CC,'--')
xlabel('Time [hours]'), ylabel('C [moles/L]')
legend('C_A', 'C_B', 'C_C')
```