CBE 60546
Fall 2021
In class test
11/12/21

1. Comparison of reactor configurations. (65 points)

A 1000 liter batch reactor has been used for many years for an *A*—>*M* isomerization. All that is "known" about the kinetics is that once the reaction temperature of 50C is reached, the concentration of *A* is reduced to 10% of its original value (which is 5 moles/liter) after 5000 seconds.

a. Assuming the simplest possible kinetics, find an expression that predicts the concentration of *A* at any time in the reactor.
b. The normal procedure is that the reactor is stopped after 5000 seconds. The reactor is drained and refilled which also takes 5000 seconds. Assuming that this done continuously all day, every day, what is the production of *M* in moles/time from this reactor?
c. With only this information, what flow of *A* feed and what size of reactor are needed if you want to produce the same amount of *A* per time in a CSTR? Pick the exit condition of the CSTR to match the batch reactor at the end of a batch (i.e., 0.5 mol/l).
d. Compare the volumes of the batch and CSTR reactors. Is this result (i.e., one of the volumes larger than the other) likely to be generally true or only because of the specific numbers of this problem?
e. You suspect that the kinetics are actually not always first order. (The small amount of "secret catalyst" which is needed certainly adds to this thinking.). A nominal "guess" for a possible kinetic expression is:

$$r_A = \frac{k_1 C_A}{K_m + k_2 C_A}$$

If this is the actual expression, explain any need to change the sizing of your CSTR.

f. Give one simple experiment that would improve the accuracy of the CSTR sizing.

2. (Very) simplified model of a virus vaccine. (35 points)

In

A simplified mathematical-computational model of the immune response to the yellow fever vaccine

C.R.B. Bonin [a*], G.C. Fernandes [b] R.W. dos Santos [a] and M.Lobosco [a]

978-1-5090-3050-7/17/$31.00 ©2017 IEEE

the authors model the yellow-fever vaccine after injection into humans. Their simplified model uses 10 equations instead of the 19 for previous models. They are able to fit the time shortly after the initial inoculation (a few weeks — bottom figure) and then the slow decay of the desired antibodies over a little more than a decade. This long decay is remarkably linear as shown just below.)

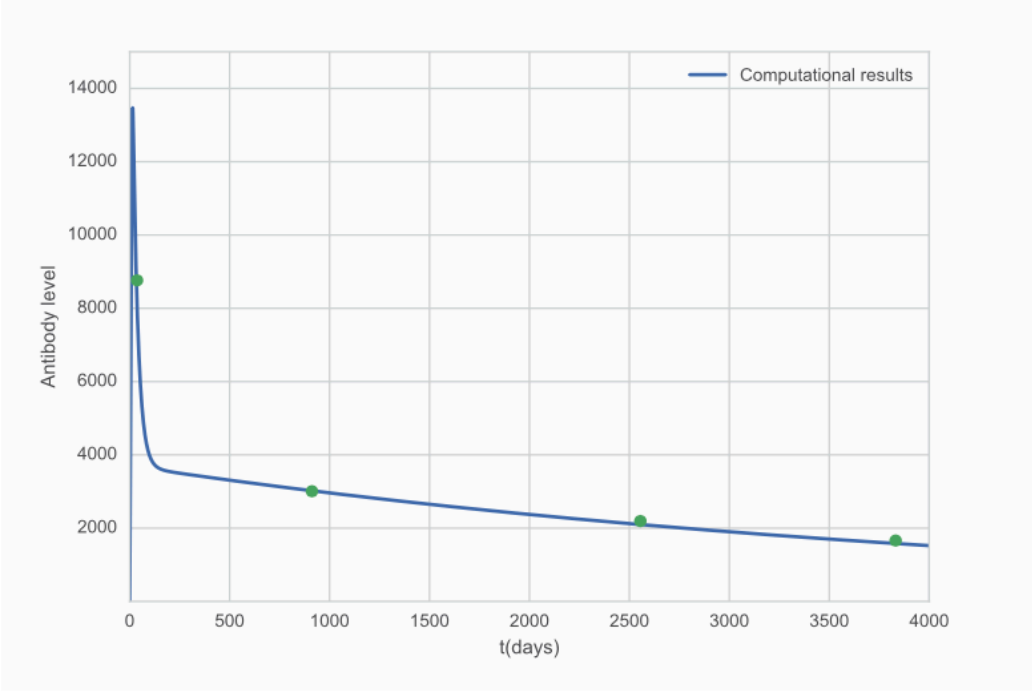


Fig. 2. Antibody curve obtained by the model (line) and experimental data extracted from the literature[34] (dots).

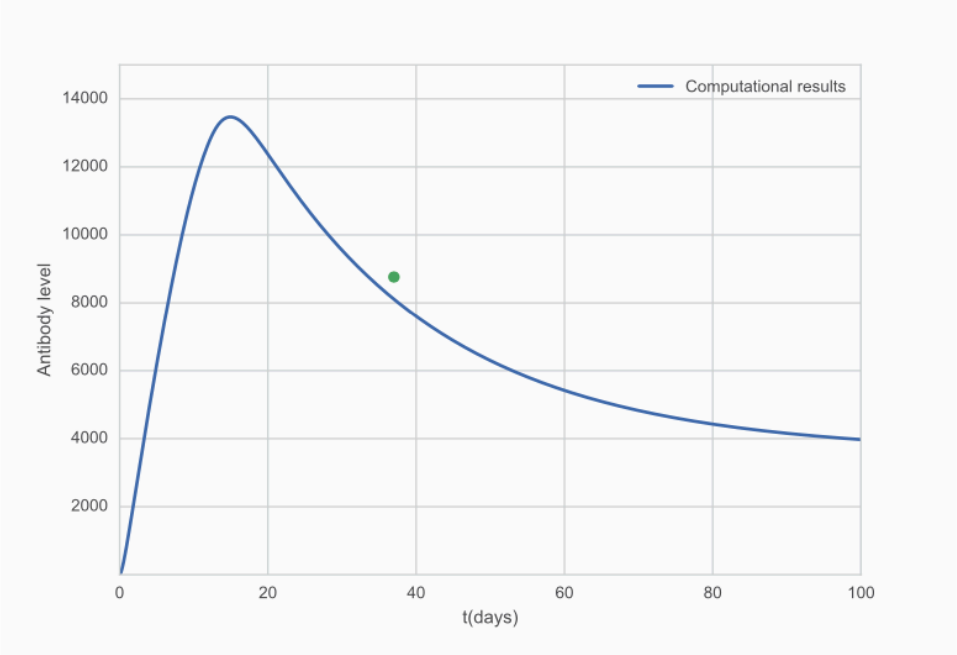


Fig. 1. Antibody curve obtained by the model (line) and experimental data extracted from the literature[34] (dot).

Consider this process as

Virus —> plasma cells —> Antibodies

V -> P -> A

as sequential reactions. If we write

$$\frac{dV}{dt} = -\alpha V$$

$$\frac{dP}{dt} = k_1 V - k_2 P$$

$$\frac{dA}{dt} = k_2 P - k_3 A$$

Then the solution is

```
In[•]:= DSolve[{D[V[t], t] == -α V[t], D[P[t], t] == k1 V[t] - k2 P[t],
    D[A[t], t] == k2 P[t] - k3 A[t], P[0] == 0, A[0] == 0, V[0] == v0}, {V[t], P[t], A[t]},
   t]
```

$$\text{Out[•]= } \left\{\left\{A[t] \to \frac{e^{-k2\,t-k3\,t-t\,\alpha}\,k1\,k2\,v0\left(e^{k2\,t+k3\,t}\,k2 - e^{k2\,t+t\,\alpha}\,k2 - e^{k2\,t+k3\,t}\,k3 + e^{k3\,t+t\,\alpha}\,k3 + e^{k2\,t+t\,\alpha}\,\alpha - e^{k3\,t+t\,\alpha}\,\alpha\right)}{(k2-k3)\,(k2-\alpha)\,(k3-\alpha)},\right.\right.$$

$$\left.\left.P[t] \to -\frac{e^{-k2\,t-t\,\alpha}\left(-e^{k2\,t}+e^{t\,\alpha}\right)k1\,v0}{k2-\alpha},\ V[t] \to e^{-t\,\alpha}\,v0\right\}\right\}$$

Or assigning the expressions.

```
In[•]:= virus = V[t] /. %50[[1]]
```

$$\text{Out}[\bullet]= e^{-t\,\alpha}\,v0$$

```
In[•]:= plasmacell = FullSimplify[P[t] /. %50[[1]]]
```

$$\text{Out}[\bullet]= -\frac{\left(e^{-k2\,t}-e^{-t\,\alpha}\right)\,k1\,v0}{k2-\alpha}$$

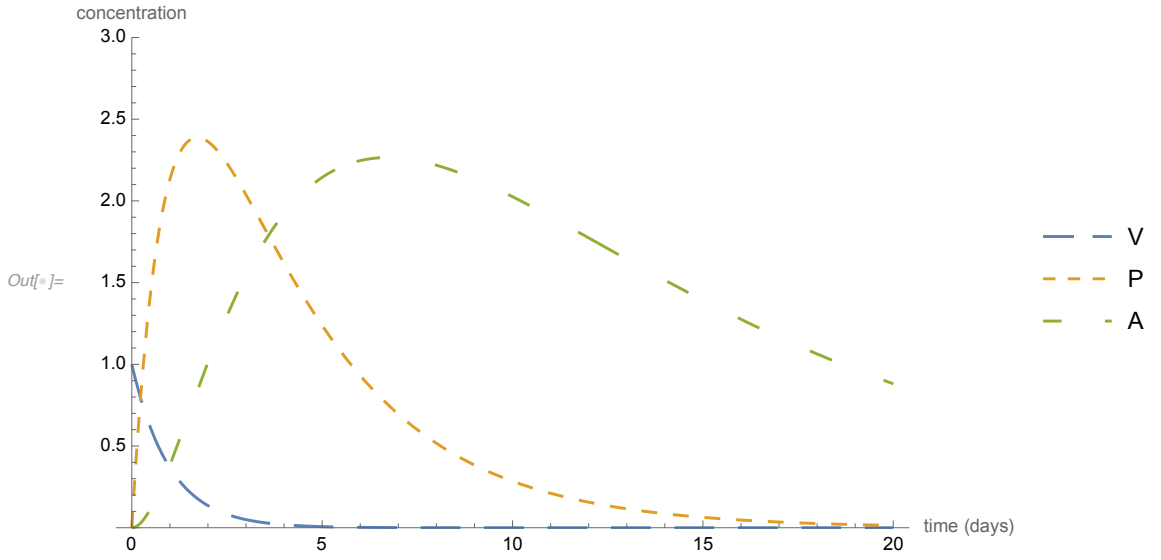
```
In[•]:= antibody = FullSimplify[A[t] /. %50[[1]]]
```

$$\text{Out}[\bullet]= \frac{e^{-t\,(k2+k3+\alpha)}\,k1\,k2\,v0\left(e^{(k2+k3)\,t}\,(k2-k3)+e^{t\,(k3+\alpha)}\,(k3-\alpha)+e^{t\,(k2+\alpha)}\,(-k2+\alpha)\right)}{(k2-k3)\,(k2-\alpha)\,(k3-\alpha)}$$

A plot for nominal numbers is:

```
In[•]:= Plot[{virus /. {α → 1, k3 → .1, k2 → .3, k1 → 4, v0 → 1},
   plasmacell /. {α → 1, k3 → .1, k2 → .3, k1 → 4, v0 → 1},
   antibody /. {α → 1, k3 → .1, k2 → .3, k1 → 4, v0 → 1}}, {t, 0, 20}, PlotRange → {0, 3},
  AxesLabel → {"time (days)", "concentration"}, PlotLegends → {"V", "P", "A"},
  PlotStyle → { Dashing[{.05, .03}], Dashing[{.02, .02}], Dashing[{.03, .07}]}]
```

Out[•]=



a. Will this model give the long linear tail seen in figure 2 above? If not, what modification to the ode's would be needed?
b. Find an expression for the time of the peak for the plasma cells.

c. One concern with vaccination is an antibody level that peaks at too high of a value which could cause medical complications. With reference to the mathematical model, what could be done to reduce this peak?
d. How could you reduce the antibody peak without causing a decrease to the long term antibody level?
e. What is the significance of the α/k_1ratio?

Please note: This very simple model is cannot and is not intended to exactly predict the behavior that would occur after administration of this vaccine. However, the same is likely true for even the most sophisticated models of complex living or natural systems. What the modeling can uncover is possible behavior scenarios which were not directly observable (for example the value of the intermediate peaks) and lead to possible “testable” hypotheses or reduce the need of the total number of experiments — possibly on humans

rate of accumulation of reactant A within the reactor = − rate of disappearance of reactant A within the reactor by chemical reaction (8.1.1)

The accumulation term is just the time derivative of the number of moles of reactant A contained within the reactor (dN_A/dt). This term may also be written in terms of either the extent of reaction ξ or the fraction conversion of the limiting reagent (f_A). (A is presumed to be the limiting reagent.) Thus,

$$\frac{dN_A}{dt} = \nu_A \frac{d\xi}{dt} = -N_{A0}\frac{df_A}{dt} \tag{8.1.2}$$

where N_{A0} is number of moles of species A present when the fraction conversion is zero.

The total rate of disappearance of reactant A is given by

$$\text{rate of disappearance of A} = (-r_A)V_R \tag{8.1.3}$$

We again emphasize that V_R is the volume physically occupied by the reacting fluid. Combination of equations (8.1.1) to (8.1.3) gives

$$N_{A0}\frac{df_A}{dt} = (-r_A)V_R \tag{8.1.4}$$

Rearrangement and integration give the general form of the design equation for a batch reactor:

$$t_2 - t_1 = N_{A0}\int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V_R} \tag{8.1.5}$$

rate of flow of reactant into volume element = Rate of flow of reactant out of volume element + rate of disappearance of reactants by chemical reactions within the volume element (8.2.1)

If the molal flow rate of reactant A into the volume element is designated as F_A, and the molal flow rate out of the volume element is represented by $F_A + dF_A$, equation

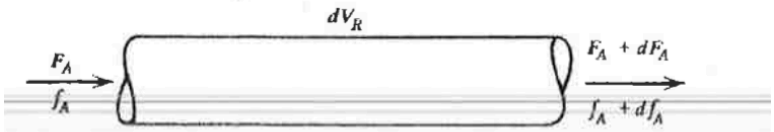


Figure 8.3 Schematic representation of differential volume element of plug flow reactor.

(8.2.1) becomes

$$F_A = (F_A + dF_A) + (-r_A)dV_R \tag{8.2.2}$$

or

$$dF_A = r_A\, dV_R \tag{8.2.3}$$

At any point the molal flow rate of reactant A can be expressed in terms of the fraction conversion f_A and the molal flow rate corresponding to zero conversion F_{A0}:

$$F_A = F_{A0}(1 - f_A) \tag{8.2.4}$$

Differentiation gives

$$dF_A = -F_{A0}\, df_A \tag{8.2.5}$$

Combination of equations (8.2.3) and (8.2.5) gives

$$\frac{dV_R}{F_{A0}} = \frac{df_A}{(-r_A)} \tag{8.2.6}$$

which may be integrated over the entire reactor volume to obtain

$$\frac{V_R}{F_{A0}} = \int_{f_{A\,in}}^{f_{A\,out}} \frac{df_A}{(-r_A)} \tag{8.2.7}$$

material balance may be written over the entire reactor. Hence,

$$\begin{pmatrix}\text{rate of flow}\\ \text{of reactant into}\\ \text{reactor}\end{pmatrix} = \begin{pmatrix}\text{rate of flow of}\\ \text{reactant out of}\\ \text{reactor}\end{pmatrix} + \begin{pmatrix}\text{rate of disappearance}\\ \text{of reactants by reaction}\\ \text{in the reactor}\end{pmatrix} \quad (8.3.1)$$

In terms of the symbols indicated in Figure 8.5,

$$F_{\text{A in}} = F_{\text{A out}} + (-r_{AF})V_R \quad (8.3.2)$$

where we again emphasize that the appropriate volume is that physically occupied by the reacting fluid. The quantity $(-r_{AF})$ is the rate of disappearance of reactant A evaluated at *reactor outlet conditions*.

Equation (8.3.2) may be rewritten in terms of the fraction conversion as

$$F_{A0}(1 - f_{\text{A in}}) = F_{A0}(1 - f_{\text{A out}}) + (-r_{AF})V_R \quad (8.3.3)$$

where F_{A0} is again the molal flow rate corresponding to zero conversion. Rearrangement gives

$$\frac{V_R}{F_{A0}} = \frac{f_{\text{A out}} - f_{\text{A in}}}{(-r_{AF})} \quad (8.3.4)$$

amount of reactant introduced into the system or relative to the amount of reactant consumed. For example, for the reaction

$$aA + bB \rightarrow rR + sS \quad (9.0.1)$$

where we take A to be the limiting reagent, the yield of species R (Y'_R) may be defined as

$$Y'_R = \frac{a(N_R - N_{R0})}{r(N_{A0} - N_A)} \quad (9.0.2)$$

where N_R and N_A are the moles of species R and A present

If the molal flow rate at zero fraction conversion is written in terms of the product of a reference volumetric flow rate $\mathcal{V}_0$ and a corresponding concentration (C_{A0}),

$$\frac{V_R}{\mathcal{V}_0} = \frac{C_{A0}(f_{\text{A out}} - f_{\text{A in}})}{(-r_{AF})} \quad (8.3.5)$$

In terms of the reactor space time,

$$\tau = \frac{C_{A0}(f_{\text{A out}} - f_{\text{A in}})}{(-r_{AF})} = \frac{C_{A0}\int_{f_{\text{A in}}}^{f_{\text{A out}}} df_A}{(-r_{AF})} \quad (8.3.6)$$

This equation differs from that for the plug flow reactor

Because one is almost always concerned with liquid-phase reactions when dealing with stirred-tank reactors, the assumption of constant fluid density is usually appropriate. In this case, for constant-density systems only, equation (8.3.6) can be written as

$$\tau = \frac{\int_{C_{\text{A in}}}^{C_{\text{A out}}} dC_A}{(r_{AF})} = \frac{C_{\text{A in}} - C_{\text{A out}}}{(-r_{AF})} \quad (8.3.7)$$

We now wish to consider some examples that indicate how to employ the foregoing equations in reactor design analyses.

For the set of first-order consecutive reactions,

$$A \xrightarrow{k_1} V \xrightarrow{k_2} W$$

determine the optimum holding time in a batch reactor and the optimum space time in a plug flow reactor in terms of

$$\frac{C_A}{C_{A0}} = e^{-k_1 t} \quad (A)$$

$$\frac{C_V}{C_{A0}} = \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (B)$$

$$\frac{C_W}{C_{A0}} = 1 - \frac{C_A}{C_{A0}} - \frac{C_V}{C_{A0}} \quad (C)$$

The time corresponding to maximum yield of V is obtained by differentiating equation (B) with respect to time and setting the derivative equal to zero:

$$\frac{d(C_V/C_{A0})}{dt} = \frac{k_1}{k_2 - k_1}(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0$$

or

$$\frac{k_1}{k_2} = e^{-(k_2 - k_1)t_{\text{optimum}}}$$

Hence, for a *plug flow* or *batch reactor*:

$$t_{\text{optimum}} = \frac{\ln(k_1/k_2)}{k_1 - k_2} = \frac{1}{k_{\text{log mean}}} \quad (D)$$

$$\frac{d N_A}{dt} = \frac{d V_R C_A}{dt} = F_{A\,in} - F_{A\,out} - r_A V_R = q_{Af} C_{Af} - q_A C_A - r_A V_R$$

r_A could be ... k C_A

correspond to zero fraction conversion. Thus,

$$\frac{V_R}{F_{A0}} = \frac{V_R}{C_{A0} v_0} = \frac{\tau}{C_{A0}} \qquad (8.2.8)$$

where we have introduced the space time τ. Combining equations (8.2.8) and (8.2.7) gives

$$\tau = \frac{V_R}{v_0} = C_{A0} \int_{f_{A\,in}}^{f_{A\,out}} \frac{df_A}{(-r_A)} \qquad (8.2.9)$$

Reactor inlet conditions