

## Chemical Reaction Engineering - Part 11 - semi-batch reactors

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### Semi-batch reactors

So far we have studied batch reactors, where there is no material flow into or out of the reactor during the reaction period.

There are situations where we want to add one reactant gradually into the reactor. This can occur for very exothermic reactions where we want to control the reaction rate by controlled addition of a reactant. This can also occur when there are multiple reactions present and we can enhance the desired reaction selectively with respect to the undesired reaction. Another reason would be to supply a gaseous reactant to a liquid-phase reaction at a constant pressure.

There are situations where we want to remove one or more of the products from the reactor during the reaction. A common situation is a liquid-phase reaction that produces gaseous products and we can vent the products from the reactor to prevent over pressuring the reactor. Removing a product can also increase conversion when conversion is limited by equilibrium.

There may also be cases where we can combine a separation unit, such as a membrane, with the reactor to enhance production of a desired product.

### Math models of semi-batch reactors

Our goal is a mathematical model that we can use for reactor analysis and design.

Previously, with a single reaction in a batch reactor, we only needed to write a component balance for our key component A. Knowing the change in A, we can use a stoichiometric table to compute the changes in all the other components in the stoichiometric equation.

So the question is, what changes occur in the math when we go to a semi-batch reactor?

The main change is that, with a semi-batch reactor, the amounts of some of the chemical components change by a process other than reaction, with that process being selective addition or removal of a component. This means that we need to write more than one component balance, even for a single reaction.

The default option is to write a component balance for all components present in the system.

Often, we can reduce the number of component balances.

For a set of two or more components whose relative amounts change only by chemical reaction, we only need to write a component balance for one of those components. Upon integration of that component balance such that we know the moles of that component in the reactor at any time, we can use stoichiometry to solve for the amounts of the other components in that set of components.

### Case 1 - non-key reactant B is fed during reaction

When reactant component A is not fed to the reactor during reaction, we can define  $X_A$  as we have before. We can write, in terms of  $X_A$ , the lines of the stoichiometric table for components that are not fed nor removed. Then write the differential component balances for A and the components that are fed or removed. We can use  $X_A$  or  $N_A$  as the dependent integration variable for the balance on A. For components that are fed or removed, add a term for the flow rate to the component balance. At any stage of integration, amounts of components other than A that are not fed nor removed can be computed using the stoichiometric table and  $X_A$ .

Consider the liquid-phase reaction  $A + B \rightarrow C + D$  where  $r_A = -kC_A C_B$ . The reactor is filled initially with a solution of A and solvent only. Starting at  $t = 0$ , a solution containing B is fed at a constant rate to the reactor and the reaction begins. We can write a stoichiometric table with A, C and D because the relative amounts of these components change only by reaction.

$$\begin{aligned}N_A &= N_{A0} - N_{A0} X_A \\N_C &= N_{C0} + N_{A0} X_A \\N_D &= N_{D0} + N_{A0} X_A\end{aligned}$$

Write component balances for A and B

$$\frac{dN_A}{dt} = r_A V$$

$$\frac{dN_B}{dt} = C_{B,\text{in}} v_{\text{in}} + r_B V$$

This relationship still holds

$$\frac{r_A}{v_A} = \frac{r_B}{v_B} \quad ; \quad \frac{r_A}{-1} = \frac{r_B}{-1} \quad ; \quad r_A = r_B$$

Before we go further, we check to see what is constant and what varies. The volume  $V$  varies with time because we are adding more liquid to the reactor.

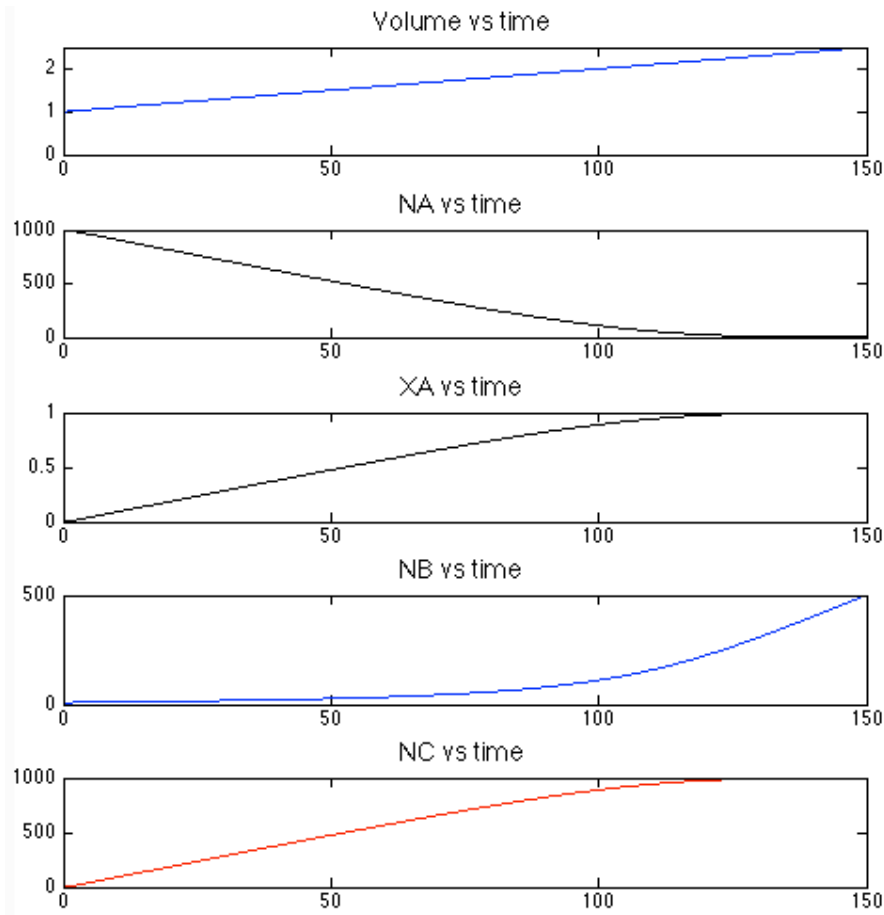
$$V = V_0 + v_{\text{in}} t$$

$$\frac{dN_A}{dt} = -k \frac{N_A}{V} \frac{N_B}{V} V = -k \frac{N_A N_B}{V_0 + v_{\text{in}} t} \quad \text{at } t = 0, N_A = N_{A0}$$

$$\frac{dN_B}{dt} = C_{B,\text{in}} v_{\text{in}} - k \frac{N_A N_B}{V_0 + v_{\text{in}} t} \quad \text{at } t = 0, N_{B0} = 0$$

We could use  $X_A$  as an integration variable instead of  $N_A$  but, since we must use  $N_B$ , we might as well use  $N_A$  for component A.

Here are plots for example parameter values.



### Case 2 - key reactant A is fed during reaction

When reactant component A is fed to the reactor, we can not use  $X_A$  as a dependent integration variable in the component balances. In this case,  $X_A$  has to be defined in terms of the integral of the moles of A added to the reactor, not in terms of the initial moles of A present. Therefore, in this case, use  $N_A$  as the dependent integration variable. At any stage of integration, we can compute  $X_A$  from the integral of the moles of A added to the reactor and the current moles of A present in the reactor.

Use the same reaction as above but now feed A instead of B. We can't write the stoichiometric table, at least in the same way we did above.

$$\frac{dN_A}{dt} = C_{A,in} v_{in} + r_A V$$

$$\frac{dN_B}{dt} = r_B V$$

$$V = V_0 + v_{in} t$$

$$\frac{dN_A}{dt} = C_{A,in} v_{in} - k \frac{N_A N_B}{V_0 + v_{in} t} \quad \text{at } t = 0, N_A = 0$$

$$\frac{dN_B}{dt} = -k \frac{N_A N_B}{V_0 + v_{in} t} \quad \text{at } t = 0, N_B = N_{B0}$$

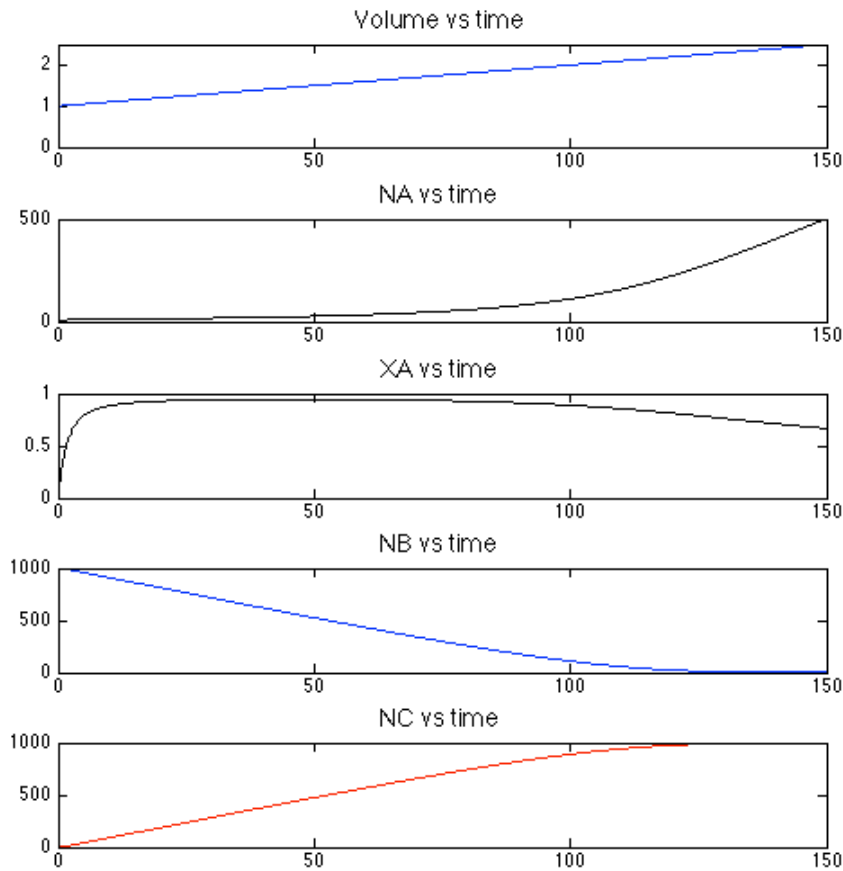
Because A is being fed to the reactor, we have to define the conversion of A so that is more general. Here,  $X_A$  at any time is the conversion of the moles of A that have been fed to the reactor up to that time.

$$N_{A,tot} = N_{A0} + \int_0^{t_{rxn}} v_{in} C_{A,in} dt$$

$$X'_A = \frac{N_{A,tot} - N_A}{N_{A,tot}}$$

$$N_{A,tot} X'_A = N_{A,tot} - N_A = \text{moles A fed to reactor that have reacted}$$

Here are plots for example parameter values. Compare  $X_A$  vs.  $t$  to the case above.



Using this definition for  $N_{i,tot}$ , the stoichiometric table for cases 1 and 2 is

$$\begin{aligned} N_A &= N_{A,tot} - N_{A0} X'_A \\ N_B &= N_{B,tot} - N_{A,tot} X'_A \\ N_C &= N_{C0} + N_{A,tot} X'_A \\ N_D &= N_{D0} + N_{A,tot} X'_A \end{aligned}$$

### Matlab script used for Cases 1 and 2

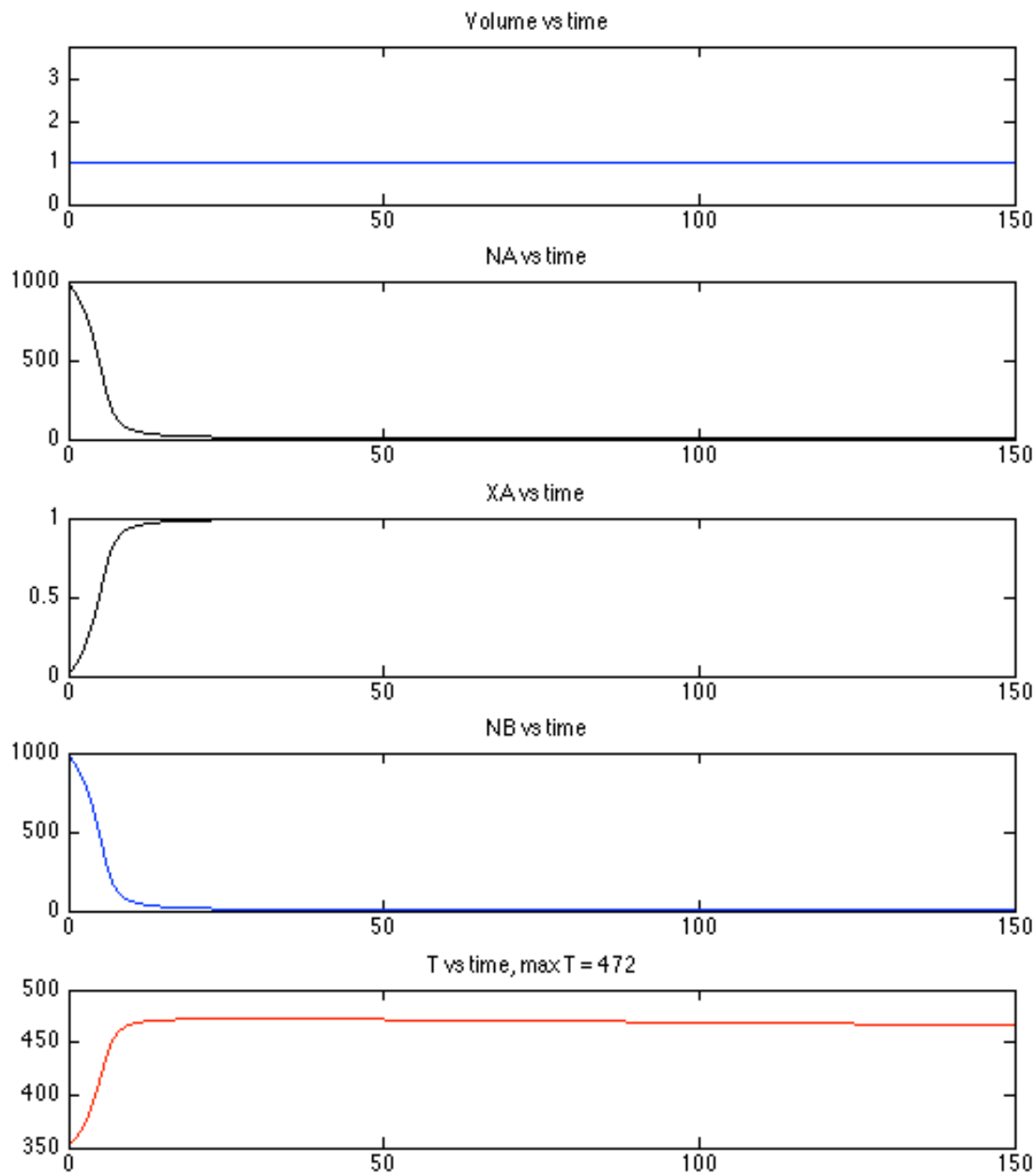
```
% semi-batch reactor
% feed A and/or B
% A + B > C + D
CA0 = 1000; % mol/m3, initial concentration of A in reactor
CB0 = 0;
V0 = 1; % m3, initial liquid volume in reactor
NA0 = CA0*V0;
NB0 = CB0*V0;
vin = 0.01; % m3/s, feed rate of solution
CAin = 0; % mol/m3 of A in feed solution
CBin = 1000; % mol/m3 of B in feed solution
k = 0.001; % m3/mol/s, rate coefficient for rA = -k*CA*CB
NA = NA0;
NB = NB0;
V = V0;
t = 0;
dt = 0.01;
tfinal = 150;
i = 1;
while t(i) < tfinal
    rate = -k*NA(i)*NB(i)/V(i);
    dNAdt = CAin*vin + rate;
    dNBdt = CBin*vin + rate;
    NA(i+1) = NA(i) + dNAdt * dt;
    NB(i+1) = NB(i) + dNBdt * dt;
    V(i+1) = V(i) + vin * dt;
    t(i+1) = t(i) + dt;
    i = i+1;
end
subplot(5,1,1), plot(t,V), title('Volume vs time')
axis([0 tfinal 0 max(V)])
subplot(5,1,2), plot(t,NA,'k'), title('NA vs time')
axis([0 tfinal 0 max(NA)])
NAtot = NA0 + CAin*vin*t;
XA = (NAtot - NA)./NAtot;
subplot(5,1,3), plot(t,XA,'k'), title('XA vs time')
axis([0 tfinal 0 1])
subplot(5,1,4), plot(t,NB,'b'), title('NB vs time')
axis([0 tfinal 0 max(NB)])
NC = 0 + NAtot.*XA; % = 0 + NAtot - NA
subplot(5,1,5), plot(t,NC,'r'), title('NC vs time')
axis([0 tfinal 0 1000])
```

### Case 3 - fed-batch with energy balance

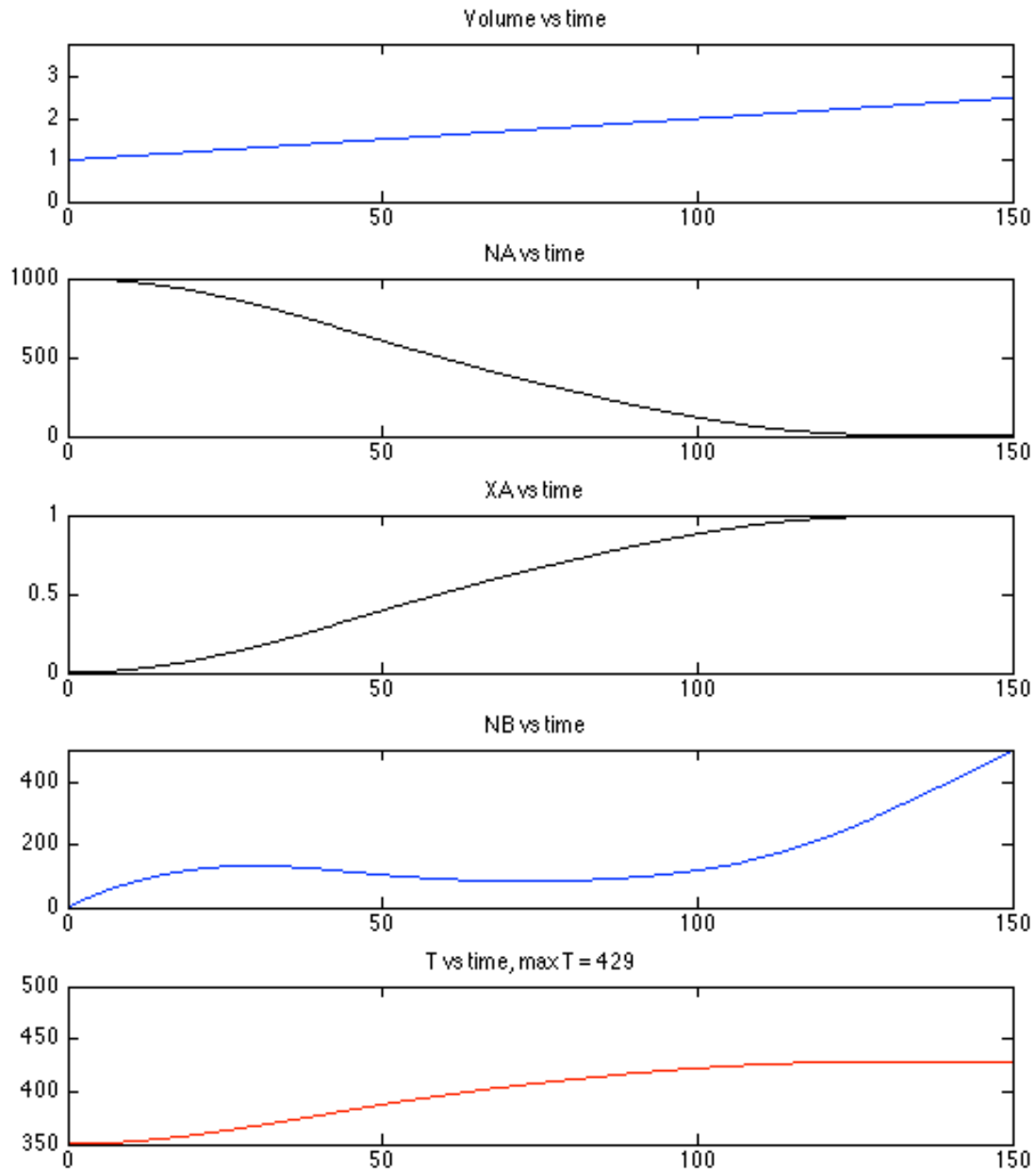
A semi-batch reactor in which a reactant is fed during the reaction is also called a fed-batch reactor. One reason to operate a reactor this way is to control heat release and the temperature for a highly exothermic reaction.

For the liquid-phase, essentially irreversible reaction  $A + B \rightarrow C + D$  with  $r_A = -kC_A C_B$ , compare the following two cases.

In the figure below, A and B are loaded into the reactor initially and there is no feed of A or B. Conversion of reactants is achieved in a short time. The maximum  $T$  is 472 K. There is a heat transfer jacket on this reactor.



Now A is loaded into the reactor initially and B is fed slowly. Now it takes longer to convert A but the maximum  $T$  is lower, 429 K.



### Matlab script used for Case 3

```
% semi-batch reactor
% feed A and/or B >> WITH ENERGY BALANCE
% A + B > C + D
CA0 = 1000; % mol/m3, initial concentration of A in reactor
CBO = 0;
V0 = 1; % m3, initial liquid volume in reactor
NA0 = CA0*V0;
NBO = CBO*V0;
vin = 0.01; % m3/s, feed rate of solution
CAin = 0; % mol/m3 of A in feed solution
CBin = 1000; % mol/m3 of B in feed solution
k300 = 3e-6; % m3/mol/s, rate coefficient at 300 K, -rA = kCACB
E = 50; % kJ/mol, activation energy
delH = -250; % kJ/mol, heat of reaction
R = 8.3145e-3; % kJ/mol/K, gas constant
Cpm = 2; % kJ/kg/K
rho = 1000; % kg/m3
UA = 1; % 10; % kJ/K/s
T0 = 350; % 350, K, initial reactor T
Tj = T0; % K, jacket T
NA = NA0;
NB = NBO;
V = V0;
T = T0;
t = 0;
dt = 0.000001/k300;
tfinal = 150;
i = 1;
while t(i) < tfinal
    k = k300*exp(-(E/R)*(1/T(i) - 1/300));
    rate = -k*NA(i)*NB(i)/V(i); % rate = rA*V = -k*CA*CB*V
    dNAdt = CAin*vin + rate;
    dNBdt = CBin*vin + rate;
    dTdt = UA*(Tj - T(i))/(rho*Cpm*V(i)) + rate*delH/(rho*Cpm*V(i));
    NA(i+1) = NA(i) + dNAdt * dt;
    NB(i+1) = NB(i) + dNBdt * dt;
    V(i+1) = V(i) + vin * dt;
    T(i+1) = T(i) + dTdt * dt;
    t(i+1) = t(i) + dt;
    i = i+1;
end
subplot(5,1,1), plot(t,V), title('Volume vs time')
axis([0 tfinal 0 3.8])
subplot(5,1,2), plot(t,NA,'k'), title('NA vs time')
axis([0 tfinal 0 max(NA)])
NAtot = NA0 + CAin*vin*t;
XA = (NAtot - NA)./NAtot;
subplot(5,1,3), plot(t,XA,'k'), title('XA vs time')
axis([0 tfinal 0 1])
subplot(5,1,4), plot(t,NB,'b'), title('NB vs time')
axis([0 tfinal 0 max(NB)])
NC = 0 + NAtot.*XA; % = 0 + NAtot - NA
tt = sprintf('T vs time, max T = %3.0f',max(T))
subplot(5,1,5), plot(t,T,'r'), title(tt)
axis([0 tfinal T0 T0+150])
```

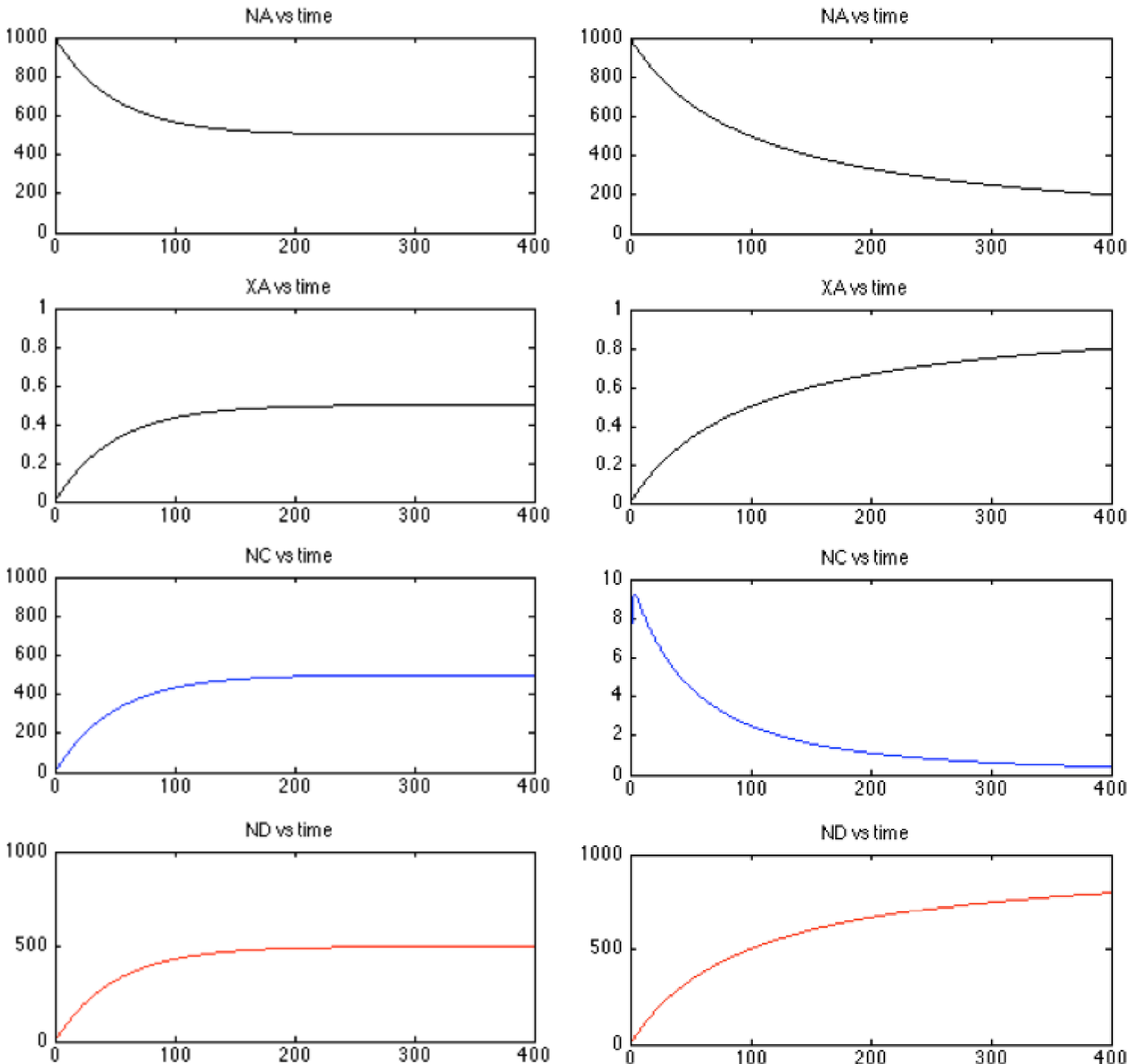


### Case 4 - selective removal of one product

Consider the liquid-phase reaction  $A + B = C + D$  where  $r_A = -k_f C_A C_B + k_b C_C C_D$ . If all components were to remain in the reactor, the conversion would be limited to the equilibrium conversion.

Now consider that product C is selectively removed from the reactor. One method to remove C would be with a selectively permeable membrane separator that is connected to the reactor with a liquid circulation loop that has a circulation rate much faster than the characteristic reaction rate. Assume that removing C has a negligible effect on the liquid volume in the reactor.

The figure on the left is the batch reactor with no C removal. The equilibrium conversion of A is 50%. The figure on the right is the semi-batch reactor with C removal. Conversion of A can approach 100% at long time. Note that the concentration scale for NC changes below from left to right.



## Matlab script for Case 4

```
% semi-batch reactor
% remove C
% A + B > C + D
clear
CA0 = 1000; % mol/m3, initial concentration of A in reactor
CB0 = 1000;
V = 1; % m3, liquid volume in reactor, assume constant
NA0 = CA0*V;
NB0 = CB0*V;
kf = 0.00001; % m3/mol/s, forward rate coefficient
kb = 0.00001; % m3/mol/s, back rate coefficient
NA = NA0;
NB = NB0;
NC = 0;
ND = 0;
alpha = 1; % (1/s), removal rate coefficient for C
t = 0;
dt = 0.01;
tfinal = 400;
i = 1;
while t(i) < tfinal
    rate = -kf*NA(i)*NB(i)/V + kb*NC(i)*ND(i)/V; % rate = rA*V
    dNAdt = rate;
    dNBdt = rate;
    dNCdt = -rate - alpha * NC(i)/V;
    dNDdt = -rate;
    NA(i+1) = NA(i) + dNAdt * dt;
    NB(i+1) = NB(i) + dNBdt * dt;
    NC(i+1) = NC(i) + dNCdt * dt;
    ND(i+1) = ND(i) + dNDdt * dt;
    t(i+1) = t(i) + dt;
    i = i+1;
end
subplot(4,1,1), plot(t,NA,'k'), title('NA vs time')
axis([0 tfinal 0 max(NA)])
XA = (NA0 - NA)/NA0;
subplot(4,1,2), plot(t,XA,'k'), title('XA vs time')
axis([0 tfinal 0 1])
subplot(4,1,3), plot(t,NC,'b'), title('NC vs time')
axis([0 tfinal 0 10])
subplot(4,1,4), plot(t,ND,'r'), title('ND vs time')
axis([0 tfinal 0 max(NA)])
```

## Additional resources

Schmidt's book - on library reserve & online via <http://roger.ucsd.edu/record=b7179459~S9>  
Chapter 3 - section 3.8

Fogler's *Essentials* book - on library reserve  
Chapter 6 - section 6.6