`CP303 — Solutions to Set #3 (July-October 2013)`

Question Bank 1:
Reaction Kinetics and Isothermal Batch Reactor Design

Solution to Q1:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A\, V \tag{3.1}$$

a) Since the reaction $A + B \longrightarrow C$ is first-order in A and zero-order in B, we could write the rate equation as

$$r_A = -k\, C_A^1\, C_B^0 = -k\, C_A \tag{3.2}$$

Combining (3.1) and (3.2), we get

$$\frac{dN_A}{dt} = -k\, C_A\, V \tag{3.3}$$

Using $N_A = C_A\, V$ along with the assumption V, the volume of the reacting mixture in the batch reactor, is a constant for a liquid-phase reaction, (3.3) could be simplified to

$$\frac{dC_A}{dt} = -k\, C_A \tag{3.4}$$

Upon integrating (3.4), we get

$$C_A = C_{Ao}\, \exp\left(-k\, t\right) \tag{3.5}$$

where C_{Ao} is the initial concentration of A in the batch reactor. Substituting $C_A = 0.5\, C_{Ao}$ at $t = 10$ min in (3.5), we get

$$0.5\, C_{Ao} = C_{Ao}\, \exp\left(-10\, k\right)$$

which gives $k = -\ln\left(0.5\right)/10 = 0.069$ min^{-1}. Using the numerical value of k in (3.5), we get

$$C_A = C_{Ao}\, \exp\left(-0.069\, t\right) \tag{3.6}$$

Equation (3.6), at $t = 20$ min, gives

$$C_A = C_{Ao}\, \exp\left(-0.069 \times 20\right) = 0.25\, C_{Ao}$$

from which we know that a quarter of A is left unreacted after 20 minutes of the commencement of the reaction.

b) Since the given reaction is first-order in A and first-order in B, we could write the rate equation as

$$r_A = -k\, C_A^1\, C_B^1 = -k\, C_A\, C_B \tag{3.7}$$

Combining (3.1) and (3.7), we get

$$\frac{dN_A}{dt} = -k\, C_A\, C_B\, V$$

which, for constant V, could be simplified to

$$\frac{dC_A}{dt} = -k\, C_A\, C_B \tag{3.8}$$

Equation (3.8) could not be integrated without relating C_B to either C_A or t. From the stoichiometry of the given reaction, we could write

$$\begin{aligned} \text{moles of } A \text{ reacted} &= \text{moles of } B \text{ reacted} \\ N_{Ao} - N_A &= N_{Bo} - N_B \end{aligned} \tag{3.9}$$

It is stated in the problem that there are equimolar quantities of A and B at the commencement of the reaction. Therefore, $N_{Ao} = N_{Bo}$, which reduces (3.9) to $N_B = N_A$. Dividing it by the volume of the reacting mixture, we get $C_B = C_A$. Substituting which in (3.8), we get

$$\frac{dC_A}{dt} = -k\, C_A^2 \tag{3.10}$$

which upon integration gives

$$\frac{1}{C_A} = \frac{1}{C_{Ao}} + k\, t \tag{3.11}$$

Substituting $C_A = 0.5\, C_{Ao}$ at $t = 10$ min in (3.11), we get $k = 0.1/C_{Ao}$ min^{-1}. Using this in (3.11), we get

$$\frac{1}{C_A} = \frac{1 + 0.1\, t}{C_{Ao}} \tag{3.12}$$

Equation (3.12), at $t = 20$ min, gives

$$C_A = C_{Ao}/3$$

from which we know that one third of A is left unreacted after 20 minutes of the commencement of the reaction.

c) Since the given reaction is second-order in A and first-order in B, the rate equation becomes

$$r_A = -k\, C_A^2\, C_B \tag{3.13}$$

Combining (3.1) and (3.13), we get

$$\frac{dN_A}{dt} = -k\, C_A^2\, C_B\, V$$

which, for constant V, could be simplified to

$$\frac{dC_A}{dt} = -k\, C_A^2\, C_B \tag{3.14}$$

Using $C_B = C_A$, which is proved in part (b), (3.14) is reduced to

$$\frac{dC_A}{dt} = -k\, C_A^3 \tag{3.15}$$

which upon integration gives

$$\frac{1}{C_A^2} = \frac{1}{C_{Ao}^2} + 2\,k\,t \tag{3.16}$$

Substituting $C_A = 0.5\, C_{Ao}$ at $t = 10$ min in (3.16), we get $k = 3/(20 \times C_{Ao}^2)$ min^{-1}. Using this in (3.16), we get

$$\frac{1}{C_A^2} = \frac{1 + 0.3\,t}{C_{Ao}^2} \tag{3.17}$$

Equation (3.17), at $t = 20$ min, gives

$$C_A = C_{Ao}/\sqrt{7} = 0.378\, C_{Ao}$$

Plot of C_A/C_{Ao} versus time for all the 3 cases analysed above is attached as Set3FigQ1.

Solution to Q2:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A\, V \tag{3.18}$$

Rate equation is given by

$$r_A = -k\, C_A\, C_B \tag{3.19}$$

Combining (3.18) and (3.19) for a constant volume batch reactor, since the reaction takes place in liquid phase, we get

$$\frac{dC_A}{dt} = -k\, C_A\, C_B \tag{3.20}$$

a) Equation (3.20) could not be integrated without relating C_B to either C_A or t. From the stoichiometry of the given reaction, one mole of A and one mole of B reacts to give 2 moles of B. Therefore, we could say that the net reaction uses one mole of A to produce one mole of B. We could therefore write

$$\begin{aligned} \text{moles of } A \text{ reacted} &= \text{moles of } B \text{ produced} \\ N_{Ao} - N_A &= N_B - N_{Bo} \end{aligned}$$

which, for a constant volume reactor, gives

$$C_{Ao} - C_A = C_B - C_{Bo}$$

Since $C_o = C_{Ao} + C_{Bo}$, the above equation could be rewritten as

$$C_B = C_o - C_A \tag{3.21}$$

Combining (3.20) and (3.21) so as to eliminate C_B, we get

$$\frac{dC_A}{dt} = -k\, C_A\, (C_o - C_A) \tag{3.22}$$

which upon integration gives

$$\begin{aligned} k\, t &= -\int \frac{dC_A}{C_A\,(C_o - C_A)} = -\frac{1}{C_o} \int \left(\frac{1}{C_A} + \frac{1}{C_o - C_A}\right) dC_A \\ &= -\frac{1}{C_o} \left[\ln C_A + \frac{\ln\,(C_o - C_A)}{-1}\right] + const \\ &= \frac{1}{C_o}\, \ln \left(\frac{C_o - C_A}{C_A}\right) + const \end{aligned} \tag{3.23}$$

Substituting $C_A = C_{Ao}$ at $t = 0$ in (3.23), we get

$$const = -\frac{1}{C_o}\, \ln \left(\frac{C_o - C_{Ao}}{C_{Ao}}\right) \tag{3.24}$$

Eliminating the $const$ from (3.23) and (3.24), we get

$$k\, C_o\, t = \ln \left[\frac{(C_o - C_A)\, C_{Ao}}{C_A\,(C_o - C_{Ao})}\right] \tag{3.25}$$

b) When the rate of reaction reaches its maximum,

$$\frac{d|r_A|}{dt} = 0 \tag{3.26}$$

Using (3.19) and (3.21) in (3.26), we get

$$\frac{d[k\, C_A\, (C_o - C_A)]}{dt} = k \left[-C_A\, \frac{dC_A}{dt} + (C_o - C_A) \frac{dC_A}{dt}\right] = k\, (C_o - 2\, C_A) \frac{dC_A}{dt} = 0$$

from which we could conclude that when the reaction rate reaches its maximum,

$$C_A = 0.5\, C_o$$

Using the above value of C_A in (3.25), we could get the time required for $|r_A|$ to reach its maximum as

$$t\Big|_{\text{at } |r_A| \text{ maximum}} = \frac{1}{k\, C_o}\, \ln \left(\frac{C_{Ao}}{C_{Bo}}\right)$$

since $C_o - C_{Ao} = C_{Bo}$.

Solution to Q3:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A\,V \tag{3.27}$$

When the reaction is assumed to be first-order in A, as stated in the problem, the rate equation becomes

$$r_A = -k\,C_A \tag{3.28}$$

Combining (3.27) and (3.28), we get

$$\frac{dN_A}{dt} = -k\,C_A\,V \tag{3.29}$$

Note: Since it is a gas-phase reaction, we shall work out the problem in terms of x_A, conversion of A, and not in terms of C_A.

Using $C_A\,V = N_A$ and $N_A = N_{Ao}(1 - x_A)$, (3.29) can be reduced to

$$\frac{dx_A}{dt} = k\,(1 - x_A) \tag{3.30}$$

a) Upon integration using the initial condition $x_A = 0$ at $t = 0$, (3.30) gives

$$k = \frac{-\ln(1 - x_A)}{t} \tag{3.31}$$

We require the value of x_A at some time during the reaction to be able to determine the numerical value of k. It is given in the problem statement that there are 80 mole% A and 20 mole% inerts initially at 1 atm, and the total pressure rises by 40% in 3 min.

We could determine the value of x_A at 3 min from the above information using

$$V = \frac{P_o}{P}\,\frac{T}{T_o}\,V_o\,(1 + \epsilon_A\,x_A) \tag{3.32}$$

where

$$\epsilon_A = \frac{N_{Ao}}{N_{To}}\left[\frac{(2+1)-(1)}{1}\right] \tag{3.33}$$

for the reaction $A \longrightarrow R + 2S$.

Since there are 80 mole% A and 20 mole% inerts initially, we get $N_{Ao}/N_{To} = 0.8$. Therefore, (3.33) gives

$$\epsilon_A = 0.8 \times 2 = 1.6 \tag{3.34}$$

Using (3.34) and the data $V = V_o$ (constant volume reactor), $T = T_o$ (isothermal condition), $P_o = 1$ atm and $P_T = 1.4$ atm (pressure rises by 40% in 3 min) in (3.32), we get

$$1 = \frac{1}{1.4}\,(1 + 1.6\,x_A)$$

which gives $x_A = 1/4$ at $t = 3$ min. Substituting which in (3.31)

$$k = \frac{-\ln(1-1/4)}{3 \text{ min}} = \frac{0.2876}{3 \text{ min}} = 0.0959 \text{ min}^{-1} \tag{3.35}$$

b) In another 3 min, i.e. when $t = 6$ min, we could determine the value of x_A from (3.31) using the numerical value of k from (3.35) as follows:

$$0.0959 = \frac{-\ln(1-x_A)}{6}$$

which gives

$$x_A = 1 - \exp(-0.0959 \times 6) = 0.4375$$

Using $x_A = 0.4375$, $V = V_o$, $T = T_o$ and $P_o = 1$ atm and $\epsilon_A = 1.6$ from (3.34), in (3.32), we get

$$P\Big|_{\text{at 6 min}} = (1 \text{ atm}) \times (1 + 1.6 \times 0.4375) = 1.7 \text{ atm}$$

Solution to Q4:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A V \tag{3.36}$$

The rate equation is given by

$$r_A = -k\,C_A \tag{3.37}$$

Combining (3.36) and (3.37), we get

$$\frac{dN_A}{dt} = -k\,C_A\,V \tag{3.38}$$

a) Since we have been asked to prove $C_A = C_{Ao}\exp(-k\,t)$, we write (3.38) in terms of C_A using $N_A = C_A V$ as

$$\frac{d(C_A V)}{dt} = k\,C_A\,V$$

which, for a constant volume reactor, becomes

$$\frac{dC_A}{dt} = k\,C_A$$

Integrating the above with the initial condition $C_A = C_{Ao}$ at $t = 0$, we get

$$C_A = C_{Ao}\exp(-k\,t) \tag{3.39}$$

b) We need to verify the assumption that the reaction is first-order in A using the 6 sets of C_A vs t values given. If the data fit (3.39) then the assumption is correct. Since (3.39) is an exponential function, we need to first convert it to get a straight line relationship, which could be done as follows:

$$-\ln C_A = k\,t - \ln C_{Ao} \tag{3.40}$$

Plot of $-\ln C_A$ versus t made using the C_A vs t data is attached as Set3FigQ4. The plot shows that the $-\ln C_A$ versus t data can be fitted by the straight line, $-\ln C_A = 0.0027\ t + 4.1352$, having $R^2 = 99.99\%$, and therefore the assumption that the reaction in first-order in A is a valid one.

The slope of the straight line gives the value of k as 0.0027 min^{-1}.

c) Applying the ideal gas equation of state to relate P to the other properties of the reacting mixture at time t, we get

$$P\,V = N_T\,R\,T \tag{3.41}$$

where $N_T = N_A + N_P + N_Q$ in usual notation.

Stoichiometry for the reaction $A \longrightarrow P + Q$ gives

$$N_{Ao} - N_A = N_P - N_{Po} = N_Q - N_{Qo}$$

which becomes

$$N_{Ao} - N_A = N_P = N_Q \tag{3.42}$$

since $N_{Po} = N_{Qo} = 0$.

Combining (3.41) and (3.42), we get $P\,V = (2\,N_{Ao} - N_A)\,R\,T$, which, for a constant volume reactor, gives

$$P = \frac{2\,N_{Ao} - N_A}{V}\,R\,T = (2\,C_{Ao} - C_A)\,R\,T$$

Note:

Solutions to **Q5**, **Q6** *and* **Q7** *are not provided since they are part of Assignment 1.*

Solution to Q8:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A\,V \tag{3.43}$$

a) The rate equation for the given elementary reversible reaction is

$$r_A = -k_1\,C_A + k_2\,C_B \tag{3.44}$$

Combining (3.43) and (3.44) for a constant volume (since it is a liquid-phase reaction) reactor, we get

$$\frac{dC_A}{dt} = -k_1\,C_A + k_2\,C_B \tag{3.45}$$

Stoichiometry for the given reversible reaction yields that when one mole of A disappears in the reaction, all of it would be converted into one mole of B. Therefore, we get $N_{Ao} - N_A = N_B - N_{Bo}$, which, since V is a constant, reduces to $C_{Ao} - C_A = C_B - C_{Bo}$ It is given that there are 2 mol/litre of A present in the reactor initially and no B. Therefore, we get

$$2 - C_A = C_B \tag{3.46}$$

Combining (3.45) and (3.46) so as to eliminate C_B, we get

$$\frac{dC_A}{dt} = -k_1\, C_A + k_2\,(2 - C_A) \tag{3.47}$$

which could be integrated as follows:

$$\begin{aligned}
\frac{dC_A}{dt} + (k_1 + k_2)\, C_A &= 2\, k_2 \\
\frac{d}{dt}\left\{C_A \exp\left[(k_1 + k_2)t\right]\right\} &= 2\, k_2 \exp\left[(k_1 + k_2)t\right] \\
C_A \exp\left[(k_1 + k_2)t\right] &= \frac{2\, k_2}{k_1 + k_2} \exp\left[(k_1 + k_2)t\right] + const \qquad (3.48)
\end{aligned}$$

Since $C_A = 2$ mol/litre at $t = 0$, (3.48) gives

$$const = 2 - \frac{2\, k_2}{k_1 + k_2} = \frac{2\, k_1}{k_1 + k_2} \tag{3.49}$$

Eliminating $const$ from (3.48) and (3.49), we get the following:

$$\begin{aligned}
C_A \exp\left[(k_1 + k_2)t\right] &= \frac{2\, k_2}{k_1 + k_2} \exp\left[(k_1 + k_2)t\right] + \frac{2\, k_1}{k_1 + k_2} \\
C_A &= \frac{2\, k_2}{k_1 + k_2} + \frac{2\, k_1}{k_1 + k_2} \exp\left[-(k_1 + k_2)\, t\right] \qquad (3.50)
\end{aligned}$$

b) The rate of reaction reaches zero value at equilibrium. Therefore, (3.44) combined with (3.46) gives

$$r_A\Big|_{\text{at equilibrium}} = -k_1\, C_{A,eqm} + k_2\,(2 - C_{A,eqm}) = 0 \tag{3.51}$$

where $C_{A,eqm}$ stands for the equilibrium concentration of A. Since $C_{A,eqm}$ is given as 0.33 mol/litre, (3.51) gives

$$\frac{k_1}{k_2} = \frac{2 - C_{A,eqm}}{C_{A,eqm}} = \frac{2 - 0.33}{0.33} = 5 \tag{3.52}$$

c) The concentration of A is said to be reduced to 1 mol/litre in 0.9 min. Substituting the above in (3.50), we get

$$1 = \frac{2\, k_2}{k_1 + k_2} + \frac{2\, k_1}{k_1 + k_2} \exp\left[-(k_1 + k_2) \times 0.9\right]$$

Since $k_1 = 5\, k_2$ from (3.52), substituting which in the above we get

$$1 = \frac{2}{6} + \frac{2 \times 5}{6} \exp\left[-6 \times k_2 \times 0.9\right]$$

which reduces to

$$k_2 = -\ln(0.4)/5.4 = 0.17 \text{ min}^{-1}$$

and therefore, we get

$$k_1 = 5\,k_2 = 5 \times 0.17 \text{ min}^{-1} = 0.85 \text{ min}^{-1}$$

Solution to Q9:

Design equation for reactant A in an ideal batch reactor is given by

$$\frac{dN_A}{dt} = r_A\,V \tag{3.53}$$

a) The rate equation for the given reversible reaction is given by

$$r_A = -k_f\,C_A\,C_B + k_b\,C_P \tag{3.54}$$

Stoichiometry for the given reversible reaction yields that one mole of A combines with one mole of B to produce one mole of P. Therefore, we get $N_{Ao} - N_A = N_{Bo} - N_B = N_P - N_{Po}$, which, since V is a constant, reduces to $C_{Ao} - C_A = C_{Bo} - C_B = C_P - C_{Po}$. Initially, there are 1 kgmol/m^3 each of A and B present in the reactor and no P. Therefore, we get

$$1 - C_A = 1 - C_B = C_P \tag{3.55}$$

Combining (3.54) and (3.55) so as to eliminate C_B and C_P, we get

$$r_A = -k_f\,C_A^2 + k_b\,(1 - C_A) \tag{3.56}$$

b) To determine k_f and k_b, (3.56) should be rewritten as follows:

$$\frac{-r_A}{C_A^2} = k_f - k_b\left(\frac{1 - C_A}{C_A^2}\right) \tag{3.57}$$

We shall then construct the data set $y = -r_A/C_A^2$ versus $x = (1 - C_A)/C_A^2$ from the C_A versus $(-r_A)$ data set provided. The slope of the best straight line fit to the y versus x data points, as per (3.57), gives $-k_b$ and the intercept of which gives k_f.

Plot of $y = -r_A/C_A^2$ versus $x = (1 - C_A)/C_A^2$ is attached as Set3FigQ9. The plot shows that the data can be fitted by the straight line, y = -0.2933 X + 1.5031, having R^2 = 98.83%.

From which, we get $k_b = 0.2933 \approx$ 0.3 per min and $k_f = 1.5031 \approx$ 1.5 m^3 per (kgmol.min).

c) Using $N_A = C_A\,V$ along with the expression for r_A from (3.56) in (3.53) and utilizing the fact V may be assumed to be a constant for a liquid-phase reaction, we get

$$\frac{dC_A}{dt} = -k_f\,C_A^2 + k_b\,(1 - C_A)$$

Substituting the numerical values of k_f and k_b in the above and integrating it from $C_A =$ 1 kgmol/m^3 at $t = 0$ to $C_A =$ 0.5 kgmol/m^3 at $t = t_f$, we get

$$t_f = \int_1^{0.5} \frac{dC_A}{-1.5\,C_A^2 - 0.3\,C_A + 0.3} = \frac{1}{1.5}\int_{0.5}^{1} \frac{1}{C_A^2 + 0.2\,C_A - 0.2}\,dC_A$$

By carrying out the above integration we could get t_f.

Solution to Q10:

a) The numerical values of the forward reaction rate constant k_1 and the backward reaction rate constant k_2 are to be determined. We therefore require two independent equations in k_1 and k_2. One equation could be obtained from the information the concentration of A drops from 0.8 mol/litre to 0.6 mol/litre in one minute, provided we first find the dependence of C_A on time. The other equation could be obtained from the information that the equilibrium concentration of A is 0.52 mol/litre.

To determine the dependence of C_A on time, let us start with the design equation for reactant A in an ideal batch reactor, which is

$$\frac{dN_A}{dt} = r_A\, V \tag{3.58}$$

and the rate equation for the given first-order reversible reaction, which is

$$r_A = -k_1\, C_A + k_2\, C_R \tag{3.59}$$

Stoichiometry for the given reversible reaction yields that when one mole of A disappears in the reaction, all of it would be converted into one mole of R. Therefore, we get $N_{Ao} - N_A = N_R - N_{Ro}$, which, since V is a constant, reduces to $C_{Ao} - C_A = C_R - C_{Ro}$. It is given that there are 0.8 mol/litre of A and 0.5 mol/litre of R present in the reactor initially. Therefore, we get

$$0.8 - C_A = C_R - 0.5 \tag{3.60}$$

Combining (3.59) and (3.60) so as to eliminate C_R, we get

$$r_A = -k_1\, C_A + k_2\, (1.3 - C_A) \tag{3.61}$$

Combining (3.58) and (3.61) so as to eliminate r_A, we get

$$\frac{dC_A}{dt} = -k_1\, C_A + k_2\, (1.3 - C_A) \tag{3.62}$$

since $N_A = C_A\, V$ and since V could be taken as a constant for a liquid-phase reaction.

Equation (3.62) could be integrated as follows:

$$\begin{aligned} \frac{dC_A}{dt} + (k_1 + k_2)\, C_A &= 1.3\, k_2 \\ \frac{d}{dt}\left\{C_A\, \exp\left[(k_1 + k_2)t\right]\right\} &= 1.3\, k_2\, \exp\left[(k_1 + k_2)t\right] \\ C_A\, \exp\left[(k_1 + k_2)t\right] &= \frac{1.3\, k_2}{k_1 + k_2}\exp\left[(k_1 + k_2)t\right] + const \qquad (3.63) \end{aligned}$$

Since $C_A = 0.8$ mol/litre at $t = 0$, (3.63) gives

$$const = 0.8 - \frac{1.3\, k_2}{k_1 + k_2} = \frac{0.8\, k_1 - 0.5\, k_2}{k_1 + k_2} \tag{3.64}$$

Eliminating $const$ from (3.63) and (3.64), we get the following:

$$\begin{aligned} C_A \exp\left[(k_1+k_2)t\right] &= \frac{1.3\,k_2}{k_1+k_2}\exp\left[(k_1+k_2)t\right] + \frac{0.8\,k_1-0.5\,k_2}{k_1+k_2} \\ C_A &= \frac{1.3\,k_2}{k_1+k_2} + \frac{0.8\,k_1-0.5\,k_2}{k_1+k_2}\exp\left[-(k_1+k_2)\,t\right] \qquad (3.65) \end{aligned}$$

Since $C_A = 0.6$ mol/litre at $t = 1$ min, (3.65) reduces to

$$0.6 = \frac{1.3\,k_2}{k_1+k_2} + \frac{0.8\,k_1-0.5\,k_2}{k_1+k_2}\exp\left[-(k_1+k_2)\right] \qquad (3.66)$$

which gives one equation relating k_1 and k_2.

It is also given in the problem statement that at equilibrium, the concentration of A is 0.52 mol/litre. Since $r_A = 0$ at equilibrium, (3.61) gives

$$r_A\Big|_{\text{at equilibrium}} = -k_1\,(0.52) + k_2\,(1.3-0.52) = 0$$

which gives

$$\frac{k_1}{k_2} = \frac{0.78}{0.52} = 1.5 \qquad (3.67)$$

Using $k_1 = 1.5\;k_2$ from (3.67) in (3.66), we get

$$0.6 = \frac{1.3}{2.5} + \frac{0.8\times 1.5 - 0.5}{2.5}\exp\left(-2.5\,k_2\right)$$

which gives $k_2 = 0.5$ min^{-1}. Substituting it in (3.67), we get $k_1 = 0.75$ min^{-1}.

The equilibrium constant K_{eq} is defined by $K_{eq} = k_1/k_2$, which as per (3.67) is 1.5. And, of course, K_{eq} has no unit in this case.

b) Since $K_{eq} = 1.5$ at 720 K, we could write

$$\exp\left(\frac{-\Delta H}{720\,R}\right) \propto 1.5 \qquad (3.68)$$

It is given in part (b) of the problem statement that $C_{eqm} = 0.520/2$ mol/liter at 630 K. Using the C_{eqm} in (3.61), we get

$$r_A\Big|_{\text{at equilibrium}} = -k_1\,(0.52/2) + k_2\,(1.3-0.52/2) = 0$$

which gives

$$K_{eq} = \frac{k_1}{k_2} = \frac{1.3-0.26}{0.26} = 4$$

Since $K_{eq} = 4$ at 630 K, we could write

$$\exp\left(\frac{-\Delta H}{630\,R}\right) \propto 4 \qquad (3.69)$$

Dividing (3.68) by (3.69), we get

$$\exp\left\{\frac{-\Delta H}{R}\left(\frac{1}{720}-\frac{1}{630}\right)\right\}=\frac{1.5}{4}$$

which gives

$$-\Delta H = 4943.4\ \text{K} \times R = 41,100\ \text{kJ/kgmol}$$

when using R = 8.314 kJ/(kgmol.K) in the above.

Solution to Q11:

a) Design equation for reactant A in an ideal batch reactor with constant volume is given by

$$\frac{dC_A}{dt}=r_A \tag{3.70}$$

The rate equation for the first-order reaction given by $A \longrightarrow B$ is

$$r_A=-k_1\,C_A \tag{3.71}$$

Combining (3.70) and (3.71) and integrating it with the initial condition $C_A = C_{Ao}$ at t = 0, we get

$$C_A=C_{Ao}\,\exp\left(-k_1 t\right) \tag{3.72}$$

To write the design equation for B, which is a product in $A \longrightarrow B$ and a reactant in $B \longrightarrow C$, let us start with the mass balance for B over the volume of the ideal batch reactor as follows:

mass of B entering the reactor during time dt
+ mass of B being generated in the reaction $A \longrightarrow B$ during time dt
= mass of B leaving the reactor during time dt
+ mass of B accumulated within the reactor during time dt
+ mass of B disappearing in the reaction $B \longrightarrow C$ during time dt

which becomes

$$0+(r_B)\Big|_{A\longrightarrow B}M_B\,V\,dt=0+d(N_B\,M_B)+(-r_B)\Big|_{B\longrightarrow C}M_B\,V\,dt \tag{3.73}$$

Removing the molar mass M_B from (3.73) and rearranging it, we get the design equation for B in an ideal batch reactor as follows:

$$\frac{dN_B}{dt}=\left\{(r_B)\Big|_{A\longrightarrow B}-(-r_B)\Big|_{B\longrightarrow C}\right\}V \tag{3.74}$$

Since $(r_B)\Big|_{A\longrightarrow B}= (-r_A)\Big|_{A\longrightarrow B}= k_1\,C_A$ and $(r_B)\Big|_{B\longrightarrow C}= -k_2\,C_B$, (3.74)could be reduced to

$$\frac{dN_B}{dt}=\left(k_1\,C_A-k_2\,C_B\right)V$$

which, for a constant volumes reactor, becomes

$$\frac{dC_B}{dt} = k_1\, C_A - k_2\, C_B \tag{3.75}$$

The stoichiometry of a series reaction could NOT be used to relate A and B. And, therefore, we shall use C_A from (3.72) in (3.75) to get a differential equation in C_B as follows:

$$\frac{dC_B}{dt} = k_1\, C_{Ao}\, \exp\left(-k_1 t\right) - k_2\, C_B \tag{3.76}$$

which could be integrated as follows:

$$\begin{aligned} \frac{dC_B}{dt} + k_2\, C_B &= k_1\, C_{Ao}\, \exp\left(-k_1 t\right) \\ \frac{d}{dt}\left\{C_B\, \exp\left(k_2\, t\right)\right\} &= k_1\, C_{Ao}\, \exp\left(-k_1\, t\right)\, \exp\left(k_2\, t\right) \\ C_B\, \exp\left(k_2\, t\right) &= \frac{k_1\, C_{Ao}}{-k_1 + k_2} \exp\left[(-k_1 + k_2)t\right] + const \qquad (3.77) \end{aligned}$$

Since $C_B = 0$ at $t = 0$, (3.77) gives

$$const = \frac{-k_1\, C_{Ao}}{-k_1 + k_2} \tag{3.78}$$

Eliminating $const$ from (3.77) and (3.78), we get the following:

$$\begin{aligned} C_B\, \exp\left(k_2\, t\right) &= \frac{k_1\, C_{Ao}}{-k_1 + k_2} \exp\left[(-k_1 + k_2)t\right] - \frac{k_1\, C_{Ao}}{-k_1 + k_2} \\ C_B &= \frac{k_1\, C_{Ao}}{-k_1 + k_2} \left(\exp\left(-k_1\, t\right) - \exp\left(-k_2\, t\right)\right) \qquad (3.79) \end{aligned}$$

b) When C_B is at its maximum, $dC_B/dt = 0$. Therefore, differentiating (3.79) and equating it to zero gives

$$k_1\, \exp\left(-k_1\, t_{opt}\right) = k_2\, \exp\left(-k_2\, t_{opt}\right) \tag{3.80}$$

where t_{opt} is the time at which C_B reaches its maximum value.

Rearranging (3.80), we get

$$t_{opt} = \frac{\ln\left(k_2/k_1\right)}{\exp\left(-k_1 + k_2\right)} = 4.5 \text{ hr}$$

since $k_1 = 0.35$ hr^{-1} and $k_2 = 0.13$ hr^{-1}. Substituting the values of t_{opt}, k_1 and k_2 in (3.79), along with $C_{Ao} = 4$ mol/m^3 and $C_{Bo} = C_{Co} = 0$, we get

$$C_B\Big|_{max} = \frac{0.35 \times 4}{-0.35 + 0.13} \left(\exp\left(-0.35 \times 4.5\right) - \exp\left(-0.13 \times 4.5\right)\right) = 2.23 \text{ mol/m}^3$$

c) C_A and C_B as functions of time are given by (3.72) and (3.79), respectively. We need to determine C_C as a function of time, which can be done as follows for a series reaction in which stoichimetry cannot be used.

The rate of change of C_A in the reactor can be obtained by combining (3.70) and (3.71) as

$$\frac{dC_A}{dt} = -k_1\, C_A \tag{3.81}$$

The rate of change of C_B in the reactor is given by (3.75).

The rate of change of C_C in the reactor can be obtained by combing the design equation for product C in an ideal batch reactor with constant volume, given as

$$\frac{dC_C}{dt} = r_C\,,$$

and the rate equation for the first-order reaction $B \longrightarrow C$, given as

$$r_C = k_2\, C_B$$

as

$$\frac{dC_C}{dt} = k_2\, C_B \tag{3.82}$$

Adding (3.81), (3.75) and (3.82) gives the following:

$$\frac{d\,(C_A + C_B + C_C)}{dt} = -k_1\, C_A + k_1\, C_A - k_2\, C_B + k_2\, C_B = 0$$

which upon integration yields

$$C_A + C_B + C_C = constant\,.$$

Intitial conditions gives $constant$ as 4 mol/m^3. Therefore,

$$C_C = (4 - C_A - C_B)\,. \tag{3.83}$$

Plot of C_A, C_B and C_C as functions of time is attached as Set3FigQ11.

Observe in the plot that the concentration of the reactant, C_A, keeps decreasing with time and the concentration of the product, C_C, keeps increasing with time. Whereas, the concentration of the intermediate component, C_B, experiences a maximum.

Note:

Solutions to **Q12** *and* **Q13** *are not provided since they are part of Assignment 1.*
