

**Question Bank 1:**  
**Reaction Kinetics and Isothermal Batch Reactor Design**

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**Solution to Q1:**

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

$$\frac{dN_A}{dt} = r_A V \quad (3.1)$$

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

$$r_A = -k C_A^1 C_B^0 = -k C_A \quad (3.2)$$

Combining (3.1) and (3.2), we get

$$\frac{dN_A}{dt} = -k C_A V \quad (3.3)$$

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

$$\frac{dC_A}{dt} = -k C_A \quad (3.4)$$

Upon integrating (3.4), we get

$$C_A = C_{A_0} \exp(-k t) \quad (3.5)$$

where  $C_{A_0}$  is the initial concentration of  $A$  in the batch reactor. Substituting  $C_A = 0.5 C_{A_0}$  at  $t = 10$  min in (3.5), we get

$$0.5 C_{A_0} = C_{A_0} \exp(-10 k)$$

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

$$C_A = C_{A_0} \exp(-0.069 t) \quad (3.6)$$

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

$$C_A = C_{A_0} \exp(-0.069 \times 20) = 0.25 C_{A_0}$$

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

$$r_A = -k C_A^1 C_B^1 = -k C_A C_B \quad (3.7)$$

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

$$\frac{dC_A}{dt} = -k C_A C_B \quad (3.8)$$

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

$$\begin{aligned} \text{moles of } A \text{ reacted} &= \text{moles of } B \text{ reacted} \\ N_{A_0} - N_A &= N_{B_0} - N_B \end{aligned} \quad (3.9)$$

It is stated in the problem that there are equimolar quantities of  $A$  and  $B$  at the commencement of the reaction. Therefore,  $N_{A_0} = N_{B_0}$ , 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

$$\frac{dC_A}{dt} = -k C_A^2 \quad (3.10)$$

which upon integration gives

$$\frac{1}{C_A} = \frac{1}{C_{A_0}} + k t \quad (3.11)$$

Substituting  $C_A = 0.5 C_{A_0}$  at  $t = 10$  min in (3.11), we get  $k = 0.1/C_{A_0} \text{ min}^{-1}$ . Using this in (3.11), we get

$$\frac{1}{C_A} = \frac{1 + 0.1 t}{C_{A_0}} \quad (3.12)$$

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

$$C_A = C_{A_0}/3$$

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

$$r_A = -k C_A^2 C_B \quad (3.13)$$

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

$$\frac{dC_A}{dt} = -k C_A^2 C_B \quad (3.14)$$

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

$$\frac{dC_A}{dt} = -k C_A^3 \quad (3.15)$$

which upon integration gives

$$\frac{1}{C_A^2} = \frac{1}{C_{Ao}^2} + 2 k t \quad (3.16)$$

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

$$\frac{1}{C_A^2} = \frac{1 + 0.3 t}{C_{Ao}^2} \quad (3.17)$$

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

$$\frac{dN_A}{dt} = r_A V \quad (3.18)$$

Rate equation is given by

$$r_A = -k C_A C_B \quad (3.19)$$

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

$$\frac{dC_A}{dt} = -k C_A C_B \quad (3.20)$$

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

$$C_B = C_o - C_A \quad (3.21)$$

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

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

which upon integration gives

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

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

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

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

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

b) When the rate of reaction reaches its maximum,

$$\frac{d|r_A|}{dt} = 0 \quad (3.26)$$

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

$$\frac{dN_A}{dt} = r_A V \quad (3.27)$$

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

$$r_A = -k C_A \quad (3.28)$$

Combining (3.27) and (3.28), we get

$$\frac{dN_A}{dt} = -k C_A V \quad (3.29)$$

**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

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

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

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

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

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

where

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

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

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

$$\epsilon_A = 0.8 \times 2 = 1.6 \quad (3.34)$$

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)

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

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

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

## Solution to Q4:

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

$$\frac{dN_A}{dt} = r_A V \quad (3.36)$$

The rate equation is given by

$$r_A = -k C_A \quad (3.37)$$

Combining (3.36) and (3.37), we get

$$\frac{dN_A}{dt} = -k C_A V \quad (3.38)$$

a) Since we have been asked to prove  $C_A = C_{A0} \exp(-kt)$ , 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  $C_A = C_{A0}$  at  $t = 0$ , we get

$$C_A = C_{A0} \exp(-kt) \quad (3.39)$$

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:

$$-\ln C_A = kt - \ln C_{A_0} \quad (3.40)$$

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 is first-order in  $A$  is a valid one.

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

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

$$PV = N_T RT \quad (3.41)$$

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

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

$$N_{A_0} - N_A = N_P - N_{P_0} = N_Q - N_{Q_0}$$

which becomes

$$N_{A_0} - N_A = N_P = N_Q \quad (3.42)$$

since  $N_{P_0} = N_{Q_0} = 0$ .

Combining (3.41) and (3.42), we get  $PV = (2N_{A_0} - N_A)RT$ , which, for a constant volume reactor, gives

$$P = \frac{2N_{A_0} - N_A}{V} RT = (2C_{A_0} - C_A) RT$$

*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

$$\frac{dN_A}{dt} = r_A V \quad (3.43)$$

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

$$r_A = -k_1 C_A + k_2 C_B \quad (3.44)$$

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

$$\frac{dC_A}{dt} = -k_1 C_A + k_2 C_B \quad (3.45)$$

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  $N_{A_0} - N_A = N_B - N_{B_0}$ , which, since  $V$  is a constant, reduces to  $C_{A_0} - C_A = C_B - C_{B_0}$ . It is given that there are 2 mol/litre of  $A$  present in the reactor initially and no  $B$ . Therefore, we get

$$2 - C_A = C_B \quad (3.46)$$

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

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

which could be integrated as follows:

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

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

$$\text{const} = 2 - \frac{2 k_2}{k_1 + k_2} = \frac{2 k_1}{k_1 + k_2} \quad (3.49)$$

Eliminating  $\text{const}$  from (3.48) and (3.49), we get the following:

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

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

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

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

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

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

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

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

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

which reduces to

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

and therefore, we get

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

## Solution to Q9:

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

$$\frac{dN_A}{dt} = r_A V \quad (3.53)$$

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

$$r_A = -k_f C_A C_B + k_b C_P \quad (3.54)$$

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  $N_{A0} - N_A = N_{B0} - N_B = N_P - N_{P0}$ , which, since  $V$  is a constant, reduces to  $C_{A0} - C_A = C_{B0} - C_B = C_P - C_{P0}$ . Initially, there are  $1 \text{ kgmol/m}^3$  each of  $A$  and  $B$  present in the reactor and no  $P$ . Therefore, we get

$$1 - C_A = 1 - C_B = C_P \quad (3.55)$$

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

$$r_A = -k_f C_A^2 + k_b(1 - C_A) \quad (3.56)$$

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

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

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  $k_f = 1.5031 \approx 1.5 \text{ m}^3$  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  $C_A = 1 \text{ kgmol/m}^3$  at  $t = 0$  to  $C_A = 0.5 \text{ kgmol/m}^3$  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

$$\frac{dN_A}{dt} = r_A V \quad (3.58)$$

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

$$r_A = -k_1 C_A + k_2 C_R \quad (3.59)$$

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  $N_{A0} - N_A = N_R - N_{R0}$ , which, since  $V$  is a constant, reduces to  $C_{A0} - C_A = C_R - C_{R0}$ . 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

$$0.8 - C_A = C_R - 0.5 \quad (3.60)$$

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

$$r_A = -k_1 C_A + k_2 (1.3 - C_A) \quad (3.61)$$

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

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

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:

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

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

$$const = 0.8 - \frac{1.3 k_2}{k_1 + k_2} = \frac{0.8 k_1 - 0.5 k_2}{k_1 + k_2} \quad (3.64)$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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  $R = 8.314 \text{ kJ/(kgmol.K)}$  in the above.

## Solution to Q11:

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

$$\frac{dC_A}{dt} = r_A \quad (3.70)$$

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

$$r_A = -k_1 C_A \quad (3.71)$$

Combining (3.70) and (3.71) and integrating it with the initial condition  $C_A = C_{A_0}$  at  $t = 0$ , we get

$$C_A = C_{A_0} \exp(-k_1 t) \quad (3.72)$$

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

$$\begin{aligned} & \text{mass of } B \text{ entering the reactor during time } dt \\ & + \text{mass of } B \text{ being generated in the reaction } A \rightarrow B \text{ during time } dt \\ & = \text{mass of } B \text{ leaving the reactor during time } dt \\ & \quad + \text{mass of } B \text{ accumulated within the reactor during time } dt \\ & \quad + \text{mass of } B \text{ disappearing in the reaction } B \rightarrow C \text{ during time } dt \end{aligned}$$

which becomes

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

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:

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

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

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

which, for a constant volumes reactor, becomes

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (3.75)$$

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:

$$\frac{dC_B}{dt} = k_1 C_{Ao} \exp(-k_1 t) - k_2 C_B \quad (3.76)$$

which could be integrated as follows:

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

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

$$const = \frac{-k_1 C_{Ao}}{-k_1 + k_2} \quad (3.78)$$

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

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

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

$$k_1 \exp(-k_1 t_{opt}) = k_2 \exp(-k_2 t_{opt}) \quad (3.80)$$

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

Rearranging (3.80), we get

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

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

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

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 stoichiometry cannot be used.

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

$$\frac{dC_A}{dt} = -k_1 C_A \quad (3.81)$$

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 combining 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  $B \rightarrow C$ , given as

$$r_C = k_2 C_B$$

as

$$\frac{dC_C}{dt} = k_2 C_B \quad (3.82)$$

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

$$C_A + C_B + C_C = \text{constant}.$$

Initial conditions gives *constant* as  $4 \text{ mol/m}^3$ . Therefore,

$$C_C = (4 - C_A - C_B). \quad (3.83)$$

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.

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*Note:*

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

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