Problem 1. A CSTR of volume 0.602 liters (constant density liquid phase) is operated in which the following reaction occurs:

$$A + B \rightarrow C + D$$
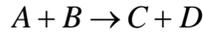
The feed rate of A is 1.16 liters/hr of a solution at concentration 5.87 mmol/L. The feed rate of B is 1.20 liters/hr at a concentration of 38.9 mmol/L. The outlet concentration of species A is 1.094 mmol/L.
Calculate the rate constant for this reaction assuming a mass-action rate law of the form:

$$r = k[A][B].$$

First draw a diagram of the problem:
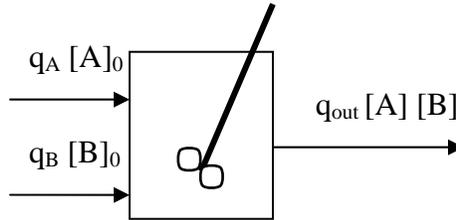
The only unknown quantities in the above figure are [B] and q_{tot}.

A volume balance on the carrier solvent gives the following relationship (constant fluid density):

$$q_A + q_B = q_{out} = 1.16\,\text{L/h} + 1.20\,\text{L/h} = 2.36\,\text{L/h}$$

Define the extent of reaction:

$$\dot{\xi} = rV \,[=]\, \frac{\text{mol}}{\text{time}}$$

A material balance on component A yields the following:

$$\frac{dn_A}{dt} = F_{A0} - F_A - \dot{\xi} = [A]_0 q_A - [A]q_{out} - \dot{\xi} \ .$$

Setting the accumulation term to zero (steady state operation) and solving for the reaction rate we find:

$$\dot{\xi} = [A]_0 q_A - [A]q_{out}$$
$$\dot{\xi} = (5.87\text{mmol/L})(1.16\text{L/h}) - (1.094\text{mmol/L})(2.36\text{L/h}) = 4.23\text{mmol/h}$$

A material balance on component B yields the following:

$$\frac{dn_B}{dt} = F_{B0} - F_B - \dot{\xi} = [B]_0 q_B - [B]q_{out} - \dot{\xi} \ .$$

Setting accumulation to zero, and solving for [B] we find:

$$[B] = \frac{[B]_0 q_B - \dot{\xi}}{q_{out}} \ .$$

$$[B] = \frac{(38.9\text{ mmol/L})(1.20\text{ L/h}) - (4.23\text{ mmol/h})}{(2.36\text{ L/h})} = 18.0\text{ mmol/L}$$

Using the given rate law and knowing the extent of reaction, we can now calculate the rate constant:

$$\dot{\xi} = rV = k[A][B]V$$
$$k = \frac{\dot{\xi}}{[A][B]V}$$
$$k = \frac{(4.23\text{ mmol/h})}{(1.094\text{ mmol/L})(18.0\text{ mmol/L})(0.602\text{ L})} = 0.357\frac{\text{L}}{\text{h mmol}} = 357 M^{-1}h^{-1}$$

Problem 2. Consider the catalyzed reaction:

$$A + B \rightarrow B + C$$
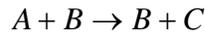
with the second-order rate constant 1.15×10^{-3} m^3/mol/ksec. The rate law is

$$r = k[A][B].$$

What volume of CSTR would be necessary to give 40% conversion of species A if the feed concentration of A is 96.5 mol/m^3, the feed concentration of B is 6.63 mol/m^3, and the flow rate is 0.5 m^3/ksec?

First draw a diagram of the problem:
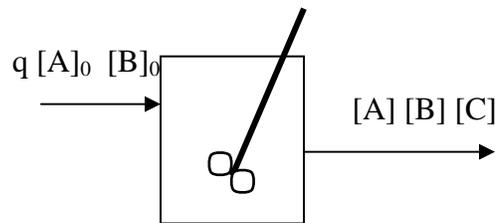
Define the extent of reaction:

$$\dot{\xi} = rV[=]\frac{\text{mol}}{\text{time}}$$

Define the conversion in terms of the variables of the problem:

$$X_A = \frac{\text{mol A reacted}}{\text{mol A fed}} = \frac{-r_A V}{q[A]_0} = \frac{\dot{\xi}}{q[A]_0}$$

A material balance on species A gives the following equation:

$$\frac{dn_A}{dt} = F_{A0} - F_A - \dot{\xi} = [A]_0 q - [A]q - \dot{\xi}$$

At steady state:

$$0 = [A]_0 q - [A]q - \dot{\xi}$$

$$\dot{\xi} = [A]_0 q - [A]q$$

Thus our conversion definition is equivalent to:

$$X_A = \frac{[A]_0 q - [A]q}{q[A]_0} = 1 - \frac{[A]}{[A]_0}$$

$$[A] = (1 - X_A)[A]_0$$

A material balance on species [B] gives the following:

$$\frac{dn_B}{dt} = F_{B0} - F_B + 0\dot{\xi} = [B]_0 q - [B]q$$

At steady state:

$$[B] = [B]_0 \ .$$

Plugging in the rate expression in the extent of reaction,

$$\dot{\xi} = rV = k[A][B]V \ ,$$

the steady state A balance becomes:

$$0 = [A]_0 q - [A]q - \dot{\xi} = ([A]_0 - [A])q - k[A][B]V \ .$$

Using the expressions derived for [B] and [A] in terms of given values, we find:

$$0 = [A]_0 X_A q - k[A]_0 (1 - X_A)[B]_0 V$$

Solving the equation for V we find:

$$V = \frac{[A]_0 X_A q}{k[A]_0 (1 - X_A)[B]_0} = \frac{X_A q}{k(1 - X_A)[B]_0}$$

$$V = \frac{(0.40)(0.5 \, \text{m}^3/\text{ksec})}{(1.15 \times 10^{-3} \, \text{m}^3/(\text{mol} \cdot \text{ksec}))(1 - 0.40)(6.63 \, \text{mol/m}^3)} = 43.7 \, \text{m}^3$$

Problem 3. Two configurations of CSTRs are contemplated for performing reversible hydrolysis of compound A to produce compounds B and C.   The forward reaction is pseudo-first-order with respect to A, with rate constant $k_1 = 1.82 \times 10^{-4}$ s^{-1}. The reverse reaction is second-order with rate constant $k_{-1} = 4.49 \times 10^{-4}$ M^{-1}s^{-1} .

(1) $A \rightarrow B + C; \quad r_1 = k_1[A]$

(2) $B + C \rightarrow A; \quad r_2 = k_{-1}[B][C]$
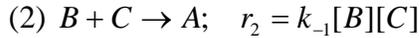
The feed is a dilute aqueous solution of A (concentration 0.25 mol/L) at a rate of 0.25 liters per hour.

Consider the following two configurations:
a) a single 15 liter CSTR.

b) three 5-liter CSTRs in series, with 75% of product species B & C selectively removed between stages 1 and 2 and between stages 2 and 3, with appropriate adjustment in flow rate; the volumetric flow rates in the two streams leaving a separator are proportional to the total number of moles of A, B, and C in each stream. See the separator diagram below.

q_0 F_{A0} F_{B0} F_{C0} q_1 F_{A1} F_{B1} F_{C1}
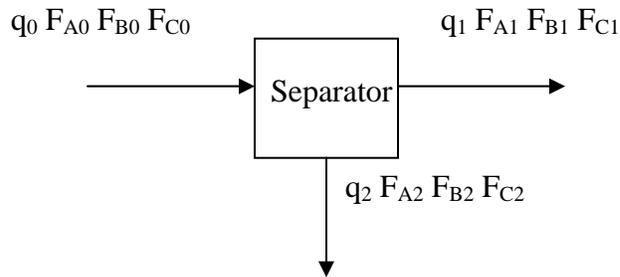
q_2 F_{A2} F_{B2} F_{C2}

If q is the volumetric flow rate and F is the molar flow rate, then the separator follows the relationships:

$$F_{A2} = 0$$
$$F_{B2} = 0.75F_{B0}$$
$$F_{C2} = 0.75F_{C0}$$
$$\frac{q_1}{q_2} = \frac{F_{A1} + F_{B1} + F_{C1}}{F_{A2} + F_{B2} + F_{C2}}$$

A full flow diagram is shown below.
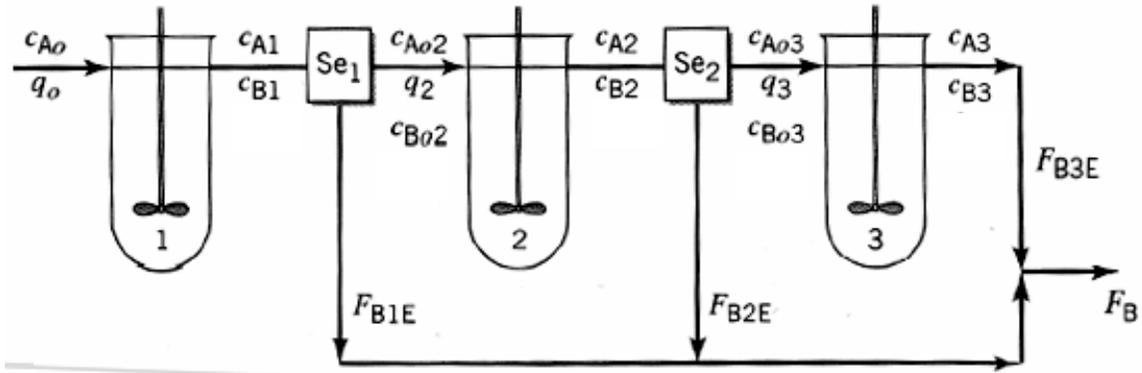
Determine the steady-state production of compound B in mol/h for options a) and b). First, consider the 1-reactor case. Draw a diagram of the situation (the control volume).

$q_0 \ [A]_0 \quad [B]_0 = [C]_0 = 0$

V=15 L

[A] [B] [C]
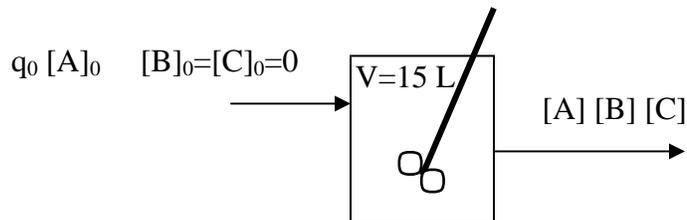
Define extents of reaction:

$$\dot{\xi}_1 = r_1 V = k_1 [A] V$$
$$\dot{\xi}_2 = r_2 V = k_{-1} [B][C] V$$

Steady state A, B, and C material balances give the following equations:

$$0 = F_{A0} - F_A - \dot{\xi}_1 + \dot{\xi}_2$$
$$0 = F_{B0} - F_B + \dot{\xi}_1 - \dot{\xi}_2$$
$$0 = F_{C0} - F_C + \dot{\xi}_1 - \dot{\xi}_2$$

These three equations can be written in terms of only three variables: [A], [B], and [C]. The system is fully specified. We must solve these equations simultaneously. The algebra is easier if we combine equations creatively to make them simpler. When you combine two equations, you keep the new equation and only one of the old ones, just as is done in linear algebra.

Notice that:
$$F_{B0} = F_{C0} = 0 .$$

Hence, subtracting the B balance equation from the C balance equation gives the result:

$$F_B = F_C$$
$$q_0[B] = q_0[C]$$
$$[B] = [C]$$

Let this new equation replace the C mole balance.

The equality of concentrations of C and B is true whenever $[C]_0$ and $[B]_0$ are equal. $[B]_0$ has been intentionally left as a variable so that the same equations derived here will also apply to the reactors in part b, where $[B]_0$ will not necessarily equal zero.

Adding together the B and A balance gives the following equation:

$$0 = F_{A0} - F_A + F_{B0} - F_B = q([A]_0 - [A] + [B]_0 - [B])$$

Dividing by q_0 and solving for [A] we get:

$$[A] = ([A]_0 + [B]_0 - [B])$$

Let this new equation replace the B mole balance.

Now we can write the A balance as a single equation with a single variable, [B] using our two new equations:

$$0 = F_{A0} - F_A - \dot{\xi}_1 + \dot{\xi}_2$$

$$0 = q_0([A]_0 - [A]) - k_1 V[A] + k_{-1} V[B][C]$$

$$0 = q_0([A]_0 - ([A]_0 + [B]_0 - [B])) - k_1 V([A]_0 + [B]_0 - [B]) + k_{-1} V[B][B]$$

$$0 = q_0[B] - q_0[B]_0 - k_1 V[A]_0 - k_1 V[B]_0 + k_1 V[B] + k_{-1} V[B]^2$$

$$0 = (k_{-1}V)[B]^2 + (q_0 + k_1 V)[B] + (-q_0[B]_0 - k_1 V[A]_0 - k_1 V[B]_0)$$

$$0 = a[B]^2 + b[B] + c$$

$$a = (k_{-1}V)$$

$$b = (q_0 + k_1 V)$$

$$c = (-q_0[B]_0 - k_1 V[A]_0 - k_1 V[B]_0)$$

This quadratic equation in [B] can be solved with the quadratic formula:

$$[B] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Since the coefficient b will always be POSITIVE, we know that we have to take the (+) root. The (-) root will always be negative. Also notice that a is always positive and c is always negative, so that the descriminant,

$$(b^2 - 4ac) > 0,$$

is always positive, and both roots are real. Hence, we may write:

$$[B] = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

with no fear of getting a negative or imaginary result.

Converting all time to hours, we find that for part a

$$a = (k_{-1}V) = (4.49 \times 10^{-4}\,\mathrm{M^{-1}s^{-1}})\left(\frac{3600\mathrm{s}}{\mathrm{h}}\right)(15\,\mathrm{L}) = 24.246\,\frac{\mathrm{L}^2}{\mathrm{mol}\cdot\mathrm{h}}$$

$$b = (q_0 + k_1 V) = (0.25\,\mathrm{L/h}) + (1.82 \times 10^{-4}\,\mathrm{s^{-1}})\left(\frac{3600\mathrm{s}}{\mathrm{h}}\right)(15\,\mathrm{L}) = 10.078\,\frac{\mathrm{L}}{\mathrm{h}}$$

$$c = (-q_0[B]_0 - k_1 V[A]_0 - k_1 V[B]_0)$$
$$c = 0 - (1.82 \times 10^{-4}\,\mathrm{s^{-1}})\left(\frac{3600\mathrm{s}}{\mathrm{h}}\right)(15\,\mathrm{L})(0.25\mathrm{M}) - 0 = -2.457\,\frac{\mathrm{mol}}{\mathrm{h}}$$

Plugging the values of the coefficients into the quadratic equation, we find:

$$[B] = 0.172\,\mathrm{M}$$

Hence, the desired production rate of B is:

$$F_B = q_0[B] = \left(0.25\frac{\text{L}}{\text{h}}\right)(0.172\,\text{M}) = 0.0430\,\text{mol/h}$$

In order to do part b, it is helpful to notice that everything flows from left to right, with no recycle loops. Hence we can solve each reactor and separator in sequence, and add up the total B recovery at the end of the process. Also, we could get it from an overall balance (a box around the entire system) once we knew the final outlet concentration of A.

For simplicity of notation, let the zero subscript refers to the current reactor feed; no subscript refers to the current reactor output.

Reactor 1
q_0=0.25L/h
$[A]_0$=0.25M
$[B]_0$=$[C]_0$=0M

V=5 L

[A] [B] [C]
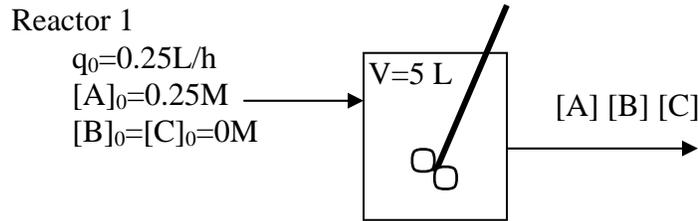
Reactor 1 follows the same relationships as the single reactor system, but with different volume. Hence the same material balances apply, and the final equation in terms of [B] is once again:

$$0 = (k_{-1}V)[B]^2 + (q_0 + k_1V)[B] + (-q_0[B]_0 - k_1V[A]_0 - k_1V[B]_0)$$

$$0 = a[B]^2 + b[B] + c$$

$$a = (k_{-1}V)$$

$$b = (q_0 + k_1V)$$

$$c = (-q_0[B]_0 - k_1V[A]_0 - k_1V[B]_0)$$

$$[B] = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

Plugging in the numbers, we find the quadratic coefficients to be:

$$a = (k_{-1}V) = (4.49 \times 10^{-4}\,\text{M}^{-1}\text{s}^{-1})\left(\frac{3600\text{s}}{\text{h}}\right)(5\,\text{L}) = 8.082\,\frac{\text{L}^2}{\text{mol}\cdot\text{h}}$$

$$b = (q_0 + k_1V) = (0.25\,\text{L/h}) + (1.82 \times 10^{-4}\,\text{s}^{-1})\left(\frac{3600\text{s}}{\text{h}}\right)(5\,\text{L}) = 3.526\,\frac{\text{L}}{\text{h}}$$

$$c = \left(-q_0[B]_0 - k_1V[A]_0 - k_1V[B]_0\right)$$

$$c = 0 - \left(1.82 \times 10^{-4}\,\text{s}^{-1}\right)\left(\frac{3600\,\text{s}}{\text{h}}\right)(5\,\text{L})(0.25\text{M}) - 0 = -0.819\,\frac{\text{mol}}{\text{h}}$$

Plugging the quadratic coefficients into the formula for [B] we find:

$$[B] = 0.168\,\text{M}$$

Using our formula for [A] in terms of [B], we find:

$$[A] = \left([A]_0 + [B]_0 - [B]\right)$$

$$[A] = 0.25\,\text{M} + 0\,\text{M} - 0.168\,\text{M} = 0.082\,\text{M}$$

Next we proceed to separator 1, carry forward our inputs, and rename our subscripted variables, so that they refer to the current separator.

q_0=0.25 L/h
[A]_0 = 0.082 M
[B]_0=[C]_0=0.168 M → Separator 1 → q_1 [A]_1 [B]_1

q_2 [A]_2 [B]_2
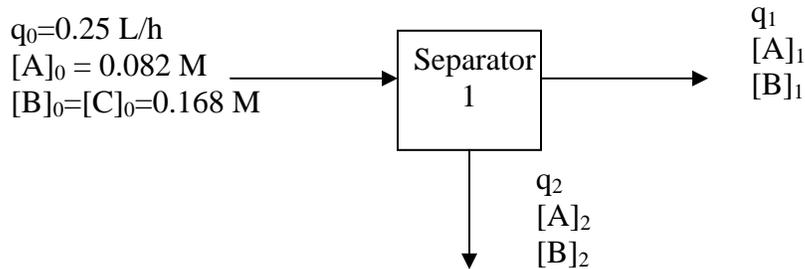
First we need to find the flow rate partitioning, then we can calculate the new concentrations from an A and B balance. (Since the separator treats B and C the same, these concentrations will continue to be equal in all streams exiting the separator.) The separator equations are:

$$F_{A2} = 0$$
$$F_{B2} = 0.75 F_{B0}$$
$$F_{C2} = 0.75 F_{C0}$$
$$\frac{q_1}{q_2} = \frac{F_{A1} + F_{B1} + F_{C1}}{F_{A2} + F_{B2} + F_{C2}}$$

Hence using the definition of molar flow rate, the knowledge that $[B]_0 = [C]_0$, and the above separator relationships, we find that:

$$\frac{q_1}{q_2} = \frac{\left(q_0[A]_0\right) + 0.25\left(q_0[B]_0\right) + 0.25\left(q_0[C]_0\right)}{0 + 0.75\left(q_0[B]_0\right) + 0.75\left(q_0[C]_0\right)} = \frac{[A]_0 + 0.5[B]_0}{1.5[B]_0}$$

$$\frac{q_1}{q_2} = \frac{[A]_0 + 0.5[B]_0}{1.5[B]_0} = \frac{(0.082) + 0.5(0.168)}{1.5(0.168)} = 0.659$$

$$q_1 = 0.659 q_2$$

Assuming a constant density liquid phase, we have a volume balance:

$$q_0 = q_1 + q_2 = 1.659 q_2$$

$$q_2 = \frac{0.25 \, \text{L/h}}{1.659} = 0.151 \, \text{L/h}$$

$$q_1 = 0.659 \times 0.151\,\text{L/h} = 0.100\,\text{L/h}$$

Thus we have recovery of product B at this stage of:

$$F_{B1E} = 0.75\big(q_0[B]_0\big) = 0.75\big(0.25\,\text{L/h}\big)\big(0.168\,\text{M}\big) = 0.0315\,\text{mol/h}$$

The last things to calculate at this step are the concentrations that are fed to the next reactor. Using the mole balance on A:

$$F_{A0} = q_0[A]_0 = F_{A1} = q_1[A]_1$$

$$[A]_1 = \frac{q_0}{q_1}[A]_0 = \frac{0.25}{0.100}\,0.082\,\frac{\text{mol}}{\text{L}} = 0.205\,\text{mol/L}\ .$$

Using the separator relationships for B and C:

$$F_{B1} = 0.25 F_{B0}$$

$$[B]_1 = 0.25\frac{q_0}{q_1}[B]_0 = 0.25\frac{0.25}{0.100}\,0.168\,\frac{\text{mol}}{\text{L}} = 0.105\,\text{mol/L}$$

$$[B]_1 = [C]_1$$

Next we proceed to reactor 2 using the results from separator 1 and rename our variables so they refer to the current reactor.
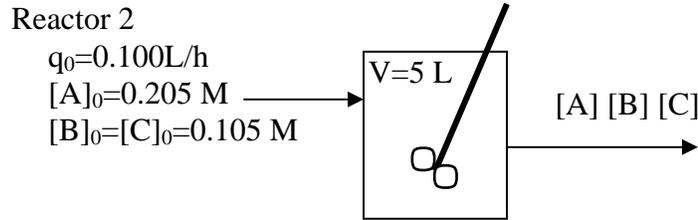
Reactor 2

$q_0 = 0.100 \text{L/h}$
$[A]_0 = 0.205 \text{ M}$
$[B]_0 = [C]_0 = 0.105 \text{ M}$

V=5 L

[A] [B] [C]

All the same equations apply with different initial concentrations and flow rates.

$$a = (k_{-1}V) = (4.49 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}) \left(\frac{3600\text{s}}{\text{h}} \right)(5\,\text{L}) = 8.082 \frac{\text{L}^2}{\text{mol} \cdot \text{h}}$$

$$b = (q_0 + k_1V) = (0.100\,\text{L/h}) + (1.82 \times 10^{-4}\text{s}^{-1}) \left(\frac{3600\text{s}}{\text{h}} \right)(5\,\text{L}) = 3.376 \frac{\text{L}}{\text{h}}$$

$$c = (-q_0[B]_0 - k_1V[A]_0 - k_1V[B]_0)$$

$$c = \left(-0.100 \frac{\text{L}}{\text{h}} \right)(0.105\text{M}) - (1.82 \times 10^{-4}\text{s}^{-1}) \left(\frac{3600\text{s}}{\text{h}} \right)(5\,\text{L})[0.205 + 0.105]\text{M}$$

$$c = -1.026 \frac{\text{mol}}{\text{h}}$$

The quadratic solution gives:

$$[B] = 0.204 \text{ M}$$

Solving for [A] from the [A]/[B] relationship we find:

$$[A] = ([A]_0 + [B]_0 - [B])$$

$$[A] = 0.205 \text{ M} + 0.105 \text{ M} - 0.204 \text{ M} = 0.106 \text{ M}$$

These concentrations will be fed to separator 2.

Next we proceed to separator 2 and rename our subscripted variables.

q_0=0.100 L/h
$[A]_0 = 0.106$ M
$[B]_0=[C]_0=0.204$ M

Separator 2

q_1
$[A]_1$
$[B]_1$

q_2
$[A]_2$
$[B]_2$
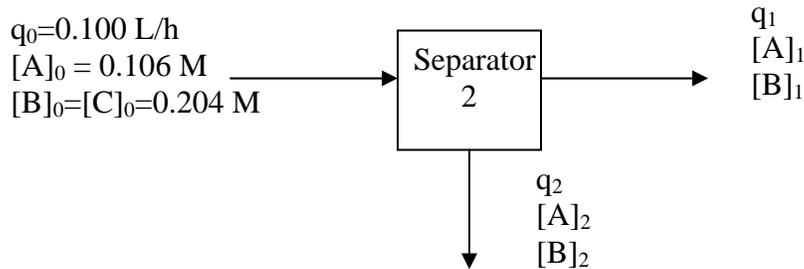
The flow rate partitioning is given by:

$$\frac{q_1}{q_2} = \frac{[A]_0 + 0.5[B]_0}{1.5[B]_0} = \frac{(0.106) + 0.5(0.204)}{1.5(0.204)} = 0.680$$

Hence, from the constant density volume balance:

$$q_2 = \frac{q_0}{1.680} = \frac{0.100\,\text{L/h}}{1.680} = 0.0595\,\text{L/h}$$

$$q_1 = q_0 - q_1 = (0.100 - 0.0595)\frac{\text{L}}{\text{h}} = 0.0405\,\text{L/h}$$

The amount of [B] recovered is:

$$F_{B2E} = 0.75(q_0[B]_0) = 0.75(0.100\text{L/h})(0.204\,\text{M}) = 0.0153\,\text{mol/h}$$

The concentrations of [A], [B], and [C] into the next reactor are:

$$F_{A0} = q_0[A]_0 = F_{A1} = q_1[A]_1$$

$$[A]_1 = \frac{q_0}{q_1}[A]_0 = \frac{0.100}{0.0405}0.106\frac{\text{mol}}{\text{L}} = 0.262\,\text{mol/L}\ .$$

$$F_{B1} = 0.25F_{B0}$$

$$[B]_1 = 0.25\frac{q_0}{q_1}[B]_0 = 0.25\frac{0.100}{0.0405}0.204\frac{\text{mol}}{\text{L}} = 0.126\,\text{mol/L}$$

$$[B]_1 = [C]_1$$

Lastly, we rename our concentrations and proceed to reactor 3.

Lastly, we proceed to reactor 3 using the results from separator 2.
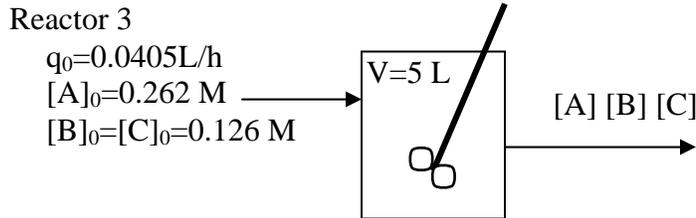
Reactor 3
q_0=0.0405L/h
[A]_0=0.262 M
[B]_0=[C]_0=0.126 M

V=5 L

[A] [B] [C]

All the same equations apply with different initial concentrations and flow rates.

$$a = (k_{-1}V) = (4.49 \times 10^{-4} M^{-1}s^{-1})\left(\frac{3600s}{h}\right)(5\,L) = 8.082\frac{L^2}{mol \cdot h}$$

$$b = (q_0 + k_1V) = (0.0405\,L/h) + (1.82 \times 10^{-4}s^{-1})\left(\frac{3600s}{h}\right)(5\,L) = 3.3165\frac{L}{h}$$

$$c = (-q_0[B]_0 - k_1V[A]_0 - k_1V[B]_0)$$

$$c = \left(-0.100\frac{L}{h}\right)(0.126M) - (1.82 \times 10^{-4}s^{-1})\left(\frac{3600s}{h}\right)(5\,L)[0.262 + 0.126]M$$

$$c = -1.284\frac{mol}{h}$$

The quadratic solution gives:

$$[B] = 0.243\,M$$

Solving for [A] from the A/B relationship equation we find:

$$[A] = ([A]_0 + [B]_0 - [B])$$
$$[A] = 0.262\,M + 0.126\,M - 0.243\,M = 0.145\,M$$

Since there is no separator, the amount of B recovered on this step is just the amount leaving the reactor:

$$F_{B3E} = [B]q_0 = (0.243\,M)\left(0.0405\frac{L}{h}\right) = 0.0098\,mol/h$$

Thus the total amount of B recovered by this path is:

$$F_B = F_{B1E} + F_{B2E} + F_{B3E} = (0.0315 + 0.0153 + 0.0098)\frac{mol}{h} = 0.0566\frac{mol}{h}$$

Another way to calculate it, and check our consistency, is to calculate the amount of B recovered from the overall A and B balances around the whole reaction system (any A that disappears must be present as B):

$$0 = F_{Ain} - F_{Aout} + F_{Bin} - F_{Bout}$$

$$F_{Bout} = F_{Ain} - F_{Aout} = \left(0.25\frac{L}{h}\right)(0.25M) - \left(0.0405\frac{L}{h}\right)(0.145M) = 0.0566\frac{mol}{h}$$

From the agreement of the numbers, it appears that mass was conserved overall.

Notice that incorporating the selective separation process to remove product along the way, the amount of B recovered was improved with the same total volume of reactor.

Due to the truncation error and numerical rounding, accept any answers within 2% of these values.

$$F_{B,3rctr} = (0.0566 \pm 0.0011)\frac{mol}{h}$$

$$F_{B,1rctr} = (0.0430 \pm 0.0009)\frac{mol}{h}$$

The modular setup of this problem (reactor units, separator units) makes a Matlab implementation straightforward. See included Matlab m-file hw3prob3.