

P4.1

At low conversions in the reactor, unreacted reactants in the reactor outlet are usually recycled to the reactor feed. However, if there are inert contaminants in the fresh feed or if there are byproducts of the reaction that are not easily separated from the recycled reactants, these will build up if recycled. Purge is a way to eliminate inert contaminants or byproducts without requiring difficult separations. The disadvantage of purge is that some of the reactants are purged as well.

P4.2

Some possibilities:

1. Combustion of natural gas (for heat or cooking): high temperature, no catalyst
2. Metabolism of glucose: catalyst (enzyme)
3. Combustion of gasoline (for transportation): high temperature
4. Catalytic converter (in automobile, for converting any unreacted gasoline or CO in exhaust fumes): catalyst
5. Catabolism of proteins: catalyst (enzyme)

P4.3

The balanced chemical equation is $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$.

The ratio of the stoichiometric coefficients is $\frac{v_{\text{O}_2}}{v_{\text{C}_3\text{H}_8}} = \frac{5}{1} = 5$, while the feed is $\frac{n_{\text{O}_2}}{n_{\text{C}_3\text{H}_8}} = \frac{6}{1} = 6$.

Therefore, oxygen is the excess reactant, and propane is the limiting reactant. The % excess oxygen is $\frac{6-5}{5} \times 100\% = 20\%$.

P4.4

The balanced chemical equation is $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$. If we assume the gases are ideal, then the molar flow rate is proportional to the volumetric flow rate. Therefore, since the stoichiometric ratio of oxygen to methane is 2:1, the stoichiometric feed rate of oxygen would be

$\frac{2}{1} \times 60 = 120 \text{ L/min O}_2$. Since the oxygen is fed at 40% excess, the oxygen feed rate must be

$1.4(120) = 168 \text{ L/min O}_2$. Since air is 21 mol% oxygen, the air feed rate is

$$\frac{168 \text{ L O}_2/\text{min}}{0.21 \text{ L air/L O}_2} = 800 \text{ L air/min}.$$

P4.5

$$f_{cA} = \frac{-v_A \xi}{n_{A,in}} = \frac{2\xi}{100} = 0.5. \text{ Therefore, } \xi = 25 \text{ gmol.}$$

$$f_{cB} = \frac{-v_B \xi}{n_{B,in}} = \frac{(1)25}{100} = 0.25$$

P4.6

$$f_{cA} = \frac{-\sum v_{Ak} \xi_k}{n_{A,in}} = \frac{2\xi_1 + \xi_2}{100} = 0.6$$

$$f_{cB} = \frac{-\sum v_{Bk} \xi_k}{n_{A,in}} = \frac{\xi_1}{100} = 0.25$$

Solving, we find

$$\xi_1 = 25$$

$$\xi_2 = 10$$

Yield of C from A is

$$y_{A \rightarrow C} = \frac{-v_{A1}}{v_{C1}} \frac{\sum v_{Ck} \xi_k}{n_{A,fed}} = \frac{2}{1} \left(\frac{\xi_1 - \xi_2}{n_{A,fed}} \right) = 2 \left(\frac{25 - 10}{100} \right) = 0.30$$

Selectivity of converting A to C is

$$s_{A \rightarrow C} = \frac{-v_{A1}}{v_{C1}} \frac{\sum v_{Ck} \xi_k}{\sum v_{Ak} \xi_k} = \frac{2}{1} \left(\frac{\xi_1 - \xi_2}{2\xi_1 + \xi_2} \right) = 2 \left(\frac{25 - 10}{50 + 10} \right) = 0.50$$

Check if yield = conversion times selectivity: $0.6 \times 0.5 = 0.3$ – yes!

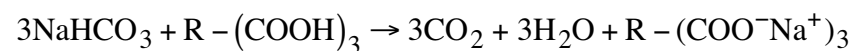
P4.7

Glucose conversion is limited by chemical reaction equilibrium. As is typical for isomerization reactions, with roughly 50% conversion at equilibrium, $f_{Cg} = \frac{\xi}{n_{g,in}} = 0.5$, $K_a \approx \frac{\xi}{1 - \xi} \approx 1$ and

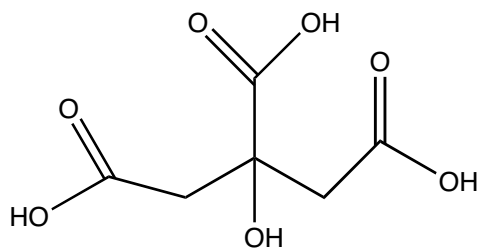
since $K_a = \exp\left(\frac{-\Delta \hat{G}_r^\circ}{RT}\right) \approx 1$, therefore $\Delta \hat{G}_r^\circ \approx 0$.

P4.8

The balanced reaction can be seen most easily if we write



where $\text{R} - (\text{COOH})_3$ is citric acid



and $\text{R}-(\text{COO}^-\text{Na}^+)_3$ is the sodium salt of citric acid.

$$1904 \text{ mg} \left(\frac{1 \text{ mmol}}{84 \text{ mg}} \right) = 22.7 \text{ mmol NaHCO}_3$$

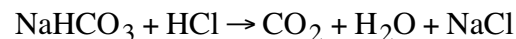
$$1000 \text{ mg} \left(\frac{1 \text{ mmol}}{192 \text{ mg}} \right) = 5.2 \text{ mmol citric acid}$$

$\frac{22.7}{5.2} = 4.36 > \frac{3}{1}$ so sodium bicarbonate is the excess reactant and citric acid is the limiting reactant.

For every mmol of citric acid that is completely neutralized, 3 mmol of CO_2 are produced. With 5.2 mmol citric acid neutralized, we produce 15.6 mmol CO_2 . If we assume the ideal gas applies, and we assume room temperature and pressure, we can calculate the volume of gas:

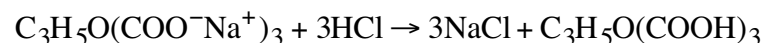
$$V = \frac{nRT}{P} = \frac{0.0156 \text{ gmol} \times 82.057 \text{ atm cm}^3 / \text{gmol K} \times 298}{1 \text{ atm}} = 380 \text{ cm}^3$$

If the citric acid in the tablet is completely neutralized, then $5.2 \text{ mmol} \times 3$, or 15.6 mmol NaHCO_3 , is consumed. That leaves $22.7 - 15.6$ or 7.1 mmol NaHCO_3 . The reaction is



7.1 mmol NaHCO_3 can neutralize 7.1 mmol HCl , or 260 mg HCl .

The sodium citrate produced in the first reaction is a weak base, capable of neutralizing the strong acid HCl :

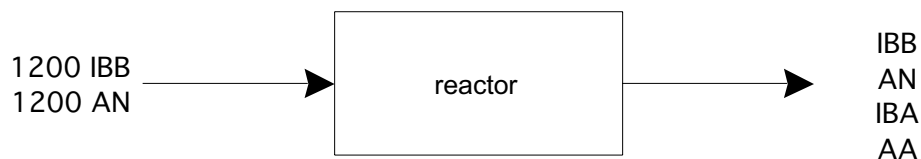


5.2 mmol sodium citrate can neutralize 15.6 mmol HCl , or 570 mg.

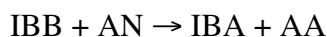
Therefore, one Alka-Seltzer can neutralize over 800 mg HCl .

P4.9

Let AN = acetic anhydride, AA = acetic acid, IBB = isobutylbenzene, and IBA = isobutylacetophenone. The flow diagram is



The stoichiometrically balanced chemical reaction is



Since the reactor operates at steady state, the material balance equations simplify to

$$\dot{n}_{\text{IBB}} = 1200 - \dot{\xi}$$

$$\dot{n}_{\text{AN}} = 1200 - \dot{\xi}$$

$$\dot{n}_{\text{IBA}} = \dot{\xi}$$

$$\dot{n}_{\text{AA}} = \dot{\xi}$$

$$\dot{n} = 2400$$

where \dot{n}_i is the molar flow rate of compound i in the reactor outlet.

From the outlet stream composition specification, we find

$$\frac{\dot{n}_{\text{AA}}}{\dot{n}} = \frac{\dot{\xi}}{2400} = 0.42$$

$$\dot{\xi} = 1008 \text{ gmol/h}$$

which is the rate of consumption of isobutylbenzene. The flow rate of IBB out of the reactor is

$$\dot{n}_{\text{IBB}} = 1200 - \dot{\xi} = 1200 - 1008 = 192 \text{ gmol/h}$$

and the fractional conversion of IBB is

$$f_{c,\text{IBB}} = \frac{\dot{\xi}}{\dot{n}_{\text{IBB},\text{in}}} = \frac{1008}{1200} = 0.84$$

P4.10

First we'll check the total mass balance:

$$\text{IN} = 134 \text{ g} + 134 \text{ g} = 268 \text{ g}$$

$$\text{OUT} = 27 \text{ g} + 52 \text{ g} + 121 \text{ g} + 68 \text{ g} = 268 \text{ g}$$

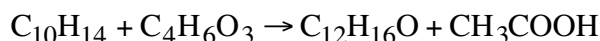
So total mass is OK.

We can proceed by either (1) checking element mass balances or (2) converting to moles, and checking stoichiometry. We will take approach 2 here.

$$\text{IN: } 134 \text{ g IBB} \times \frac{1 \text{ gmol IBB}}{134 \text{ g IBB}} = 1 \text{ gmol IBB}, 134 \text{ g AAn} \times \frac{1 \text{ gmol AAn}}{102 \text{ g AAn}} = 1.314 \text{ gmol AAn}$$

$$\text{OUT: } 27 \text{ g IBB} \times \frac{1 \text{ gmol IBB}}{134 \text{ g IBB}} = 0.20 \text{ gmol IBB}$$

Therefore, 0.80 gmol IBB are consumed by reaction. The balanced chemical reaction is

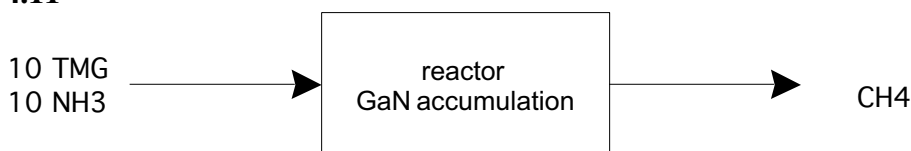


Balances on other compounds:

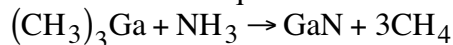
	In (moles)	Consumed or generated (moles)	Out (moles)	Molar mass	Out (grams)
$\text{C}_4\text{H}_6\text{O}_3$	1.314	-0.8	0.514	102	52.4
$\text{C}_{12}\text{H}_{16}\text{O}$	0	+0.8	+0.8	176	140.8
CH_3COOH	0	+0.8	+0.8	60	48

The last column is calculated from material balances. Agreement with the data for acetic anhydride is good, but the calculated masses of IBA and acetic acid are different from the data by 20 g. Thus, the chemist's data does not satisfy material balance requirements, and must be incorrect.

P4.11



The balanced chemical equation is



Since only methane is in the exit gas, all the TMG and ammonia fed to the reactor are converted to products, and

$$\dot{n}_{\text{TMG},out} = 0 = 10 - \dot{\xi}$$

$$\dot{\xi} = 10 \text{ } \mu\text{mol/h}$$

A 1 μm (0.0001 cm) thick layer of GaN, on a 1 cm by 1 cm square chip, is equivalent to:

$$1 \text{ cm} \times 1 \text{ cm} \times 10^{-4} \text{ cm} \times 6.1 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ gmol}}{84 \text{ g}} = 7.3 \mu\text{moles GaN}$$

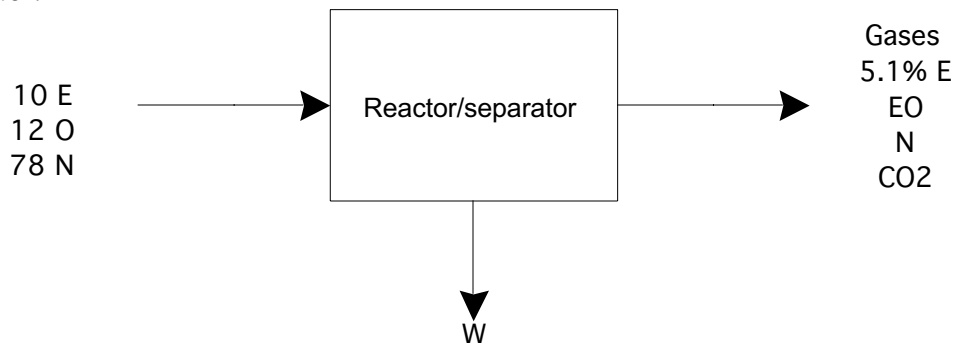
This is the total required accumulation of GaN in the system. From an integral material balance on GaN:

$$\int_0^t \dot{\xi} dt = 7.3 = \int_0^t 10 dt = 10(t - 0)$$

$$t = 0.73 \text{ h or } 44 \text{ min}$$

P4.12

A diagram of the system is shown, assuming a basis of 100 gmoles total initially charged to the reactor.



This is a batch reactor. Since there are 2 chemical reactions of known stoichiometry, we will choose compounds as components, which we indicate as E for ethylene, EO for ethylene oxide, N for N₂, O for O₂, and C for CO₂. The material balance equation for all components is:

$$n_{i,\text{sys},f} - n_{i,\text{sys},0} = \nu_{i1}\xi_1 + \nu_{i2}\xi_2$$

where $\xi_k = \int_{t_0}^{t_f} \dot{\xi}_k dt$.

For each compound, using the known initial charge to the reactor, the equations become:

$$\begin{array}{ll} 0 - 12 = -\xi_1 - 3\xi_2 & \text{or} \quad \xi_1 + 3\xi_2 = 12 \\ n_{E,\text{sys},f} - 10 = -2\xi_1 - \xi_2 & \text{or} \quad n_{E,\text{sys},f} = 10 - 2\xi_1 - \xi_2 \\ n_{N,\text{sys},f} - 78 = 0 & \text{or} \quad n_{N,\text{sys},f} = 78 \\ n_{EO,\text{sys},f} = 2\xi_1 & \\ n_{C,\text{sys},f} = 2\xi_2 & \end{array}$$

We need one more equation, which comes from the stream composition specification:

$$0.051 = \frac{n_{E,sys,f}}{n_{E,sys,f} + n_{N,sys,f} + n_{C,sys,f} + n_{EO,sys,f}} = \frac{10 - 2\xi_1 - \xi_2}{88 + \xi_2}$$

We combine to solve for the 2 extents of reaction, and from that calculate fractional conversion and yield.

$$\xi_1 = 0.8 \text{ gmol}$$

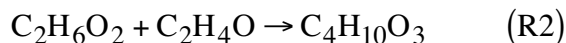
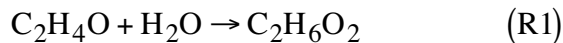
$$\xi_2 = 3.74 \text{ gmol}$$

$$f_{CE} = -\frac{-2\xi_1 - \xi_2}{n_{E,sys,0}} = \frac{2(0.8) + 3.74}{10} = 0.534$$

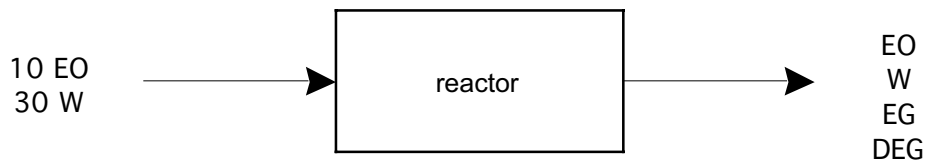
$$y_{E \rightarrow EO} = -\left(\frac{-2}{+2}\right) \frac{2\xi_1}{n_{E,sys,0}} = \frac{2(0.8)}{10} = 0.16$$

P4.13

The balanced reactions are:



Let water = W, ethylene oxide = EO, ethylene glycol = EG and diethyl glycol = DEG, then the labeled flow diagram is



with all flows given in units of gmol/min. The reactor is at assumed to be steady state. Water is the excess reactant to favor (R1) over (R2), and because it is the cheaper raw material. From conversion and selectivity specifications,

$$f_{C,EO} = \frac{-\sum_k \nu_{EO,k} \dot{\xi}_k}{\dot{n}_{EO,in}} = \frac{\dot{\xi}_1 + \dot{\xi}_2}{10} = 0.92$$

$$s_{EO \rightarrow EG} = \frac{\nu_{EO,1}}{\nu_{EG,1}} \frac{\sum_k \nu_{EG,k} \dot{\xi}_k}{\sum_k \nu_{EO,k} \dot{\xi}_k} = \frac{-1}{1} \left(\frac{\dot{\xi}_1 - \dot{\xi}_2}{-\dot{\xi}_1 - \dot{\xi}_2} \right) = \left(\frac{\dot{\xi}_1 - \dot{\xi}_2}{\dot{\xi}_1 + \dot{\xi}_2} \right) = 0.85$$

Solving, we find

$$\dot{\xi}_1 = 8.51 \text{ gmol/min}$$

$$\dot{\xi}_2 = 0.69 \text{ gmol/min}$$

From this and the material balance equations, we calculate the reactor outlet flows:

$$\dot{n}_{EO,out} = 10 - (\dot{\xi}_1 + \dot{\xi}_2) = 10 - 9.2 = 0.8 \text{ gmol/min}$$

$$\dot{n}_{W,out} = 30 - \dot{\xi}_1 = 30 - 8.51 = 21.49 \text{ gmol/min}$$

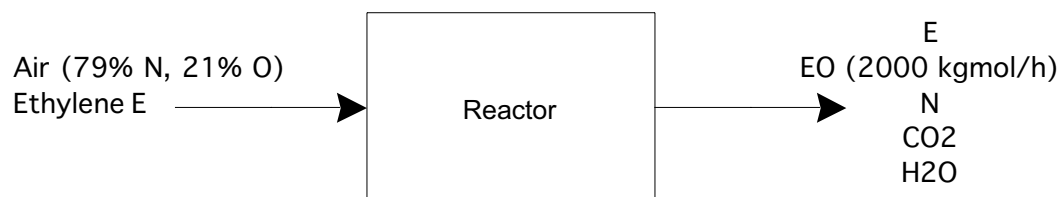
$$\dot{n}_{EG,out} = (\dot{\xi}_1 - \dot{\xi}_2) = 8.51 - 0.69 = 7.82 \text{ gmol/min}$$

$$\dot{n}_{DEG,out} = \dot{\xi}_2 = 0.69 \text{ gmol/min}$$

and we can calculate that the total molar flow out = $0.8 + 21.49 + 7.82 + 0.69 = 30.8 \text{ gmol/min}$, and the reactor outlet contains 2.6 mol% EO, 69.8 mol% W, 25.4 mol% EG, and 2.2 mol% DEG.

Yield = conversion times selectivity = $0.92 \times 0.85 = 0.78$.

P4.14



The reactor is assumed to operate in steady-state mode. There are 6 components: ethylene E, ethylene oxide EO, nitrogen N, oxygen O, water W and carbon dioxide C. The basis is given:

$$\dot{n}_{EO,out} = 2000$$

with all flows in kgmol/h.

There are two chemical reactions of known stoichiometry. A quick DOF analysis reveals that there are 8 stream variables + 2 system variables, and there are 2 stream composition specifications, 1 system performance specification, 1 specified flow, and 6 material balance equations, so $\text{DOF} = 10 - 10 = 0$ and the problem is correctly specified.

We have two specified stream compositions:

$$\frac{\dot{n}_{O,in}}{\dot{n}_{N,in}} = \frac{21}{79}, \quad \frac{\dot{n}_{E,in}}{\dot{n}_{O,in}} = \frac{2}{1}$$

and one system performance specification – fractional conversion of ethylene to products:

$$\frac{\dot{n}_{E,cons}}{\dot{n}_{E,in}} = 0.25 = \frac{2\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{E,in}}$$

The material balance equations are:

$$\begin{aligned}
 \dot{n}_{N,out} &= \dot{n}_{N,in} \\
 2000 &= 2\dot{\xi}_1 & \text{or} & \quad \dot{\xi}_1 = 1000 \\
 0 &= \dot{n}_{O,in} - \dot{\xi}_1 - 3\dot{\xi}_2 & \text{or} & \quad \dot{n}_{O,in} = 1000 + 3\dot{\xi}_2 \\
 \dot{n}_{E,out} &= \dot{n}_{E,in} - 2\dot{\xi}_1 - \dot{\xi}_2 & \text{or} & \quad \dot{n}_{E,out} = \dot{n}_{E,in} - 2(1000) - \dot{\xi}_2 \\
 \dot{n}_{C,out} &= 2\dot{\xi}_2 \\
 \dot{n}_{W,out} &= 2\dot{\xi}_2
 \end{aligned}$$

We rewrite the system performance specification to get one equation in 2 unknowns;

$$0.25\dot{n}_{E,in} = 2000 + \dot{\xi}_2$$

We combine the oxygen material balance equation with the stream composition specification to find another equation in the same 2 unknowns:

$$0.5\dot{n}_{E,in} = 1000 + 3\dot{\xi}_2$$

Now we can solve these two equations simultaneously to find:

$$\begin{aligned}
 \dot{\xi}_2 &= 3000 \\
 \dot{n}_{E,in} &= 20,000
 \end{aligned}$$

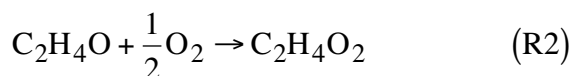
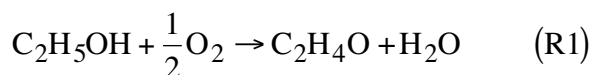
We back out the air flow rates from the stream compositions:

$$\begin{aligned}
 \dot{n}_{O,in} &= 10,000 \\
 \dot{n}_{N,in} &= 37,600
 \end{aligned}$$

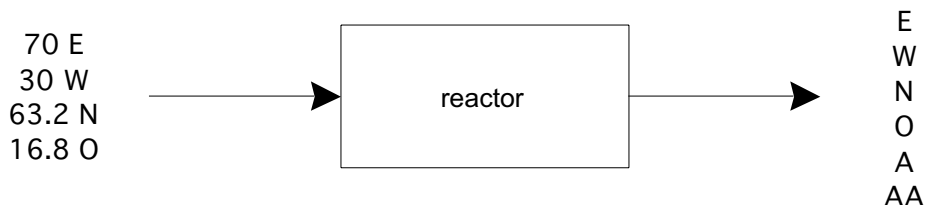
Therefore, the reactor feed is 67,600 kgmol/h, at 30 mol% ethylene, 56% N₂, and 15 mol% O₂. (we could easily calculate reactor outlet flow and composition, yield, and selectivity.)

P4.15

The two stoichiometrically balanced chemical equations are



The reactor flow diagram is (with all flow rates in gmol/min)



where E is ethanol, W is water, N is nitrogen, O is oxygen, A is acetaldehyde, and AA is acetic acid.

Since the O/E ratio in the feed is 16.8/70 or 0.24 but the stoichiometric ratio (for reaction R1 only) is 0.5, oxygen is the limiting reactant. This is chosen to reduce further oxidation of acetaldehyde to acetic acid.

At steady state, the material balances are

$$\begin{aligned}\dot{n}_{E,out} &= 70 - \dot{\xi}_1 \\ \dot{n}_{W,out} &= 30 + \dot{\xi}_1 \\ \dot{n}_{O,out} &= 16.8 - 0.5\dot{\xi}_1 - 0.5\dot{\xi}_2 = 0 \\ \dot{n}_{N,out} &= 63.2 \\ \dot{n}_{A,out} &= \dot{\xi}_1 - \dot{\xi}_2 = 25 \\ \dot{n}_{AA,out} &= \dot{\xi}_2\end{aligned}$$

where we inserted the known flow rates of oxygen and acetaldehyde in the reactor outlet. From the balances on oxygen and acetaldehyde we find the extents of reaction,

$$\begin{aligned}\dot{\xi}_1 &= 29.3 \text{ gmol/min} \\ \dot{\xi}_2 &= 4.3 \text{ gmol/min}\end{aligned}$$

which then allows us to solve for the reactor outlet stream composition and flow rate,

$$\begin{aligned}\dot{n}_{E,out} &= 70 - 29.3 = 40.7 \text{ gmol/min} \\ \dot{n}_{W,out} &= 30 + 29.3 = 59.3 \text{ gmol/min} \\ \dot{n}_{N,out} &= 63.2 \text{ gmol/min} \\ \dot{n}_{A,out} &= 25 \text{ gmol/min} \\ \dot{n}_{AA,out} &= 4.3 \text{ gmol/min} \\ \dot{n}_{out} &= 40.7 + 59.3 + 63.2 + 25 + 4.3 = 192.5 \text{ gmol/min}\end{aligned}$$

or, the reactor outlet contains 21 mol% E, 31 mol% W, 33 mol% N, 13 mol% A, and 2 mol% AA.

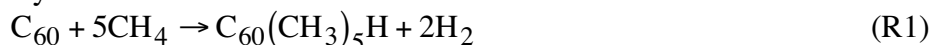
We can also calculate the fractional conversion of ethanol and yield of acetaldehyde from ethanol:

$$f_{C,E} = \frac{-\sum v_{E,k} \dot{\xi}_k}{\dot{n}_{E,in}} = \frac{\dot{\xi}_1}{70} = \frac{29.3}{70} = 0.42$$

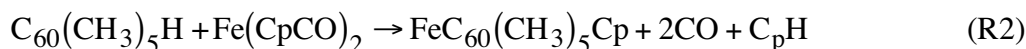
$$y_{E \rightarrow A} = \frac{-v_{A,1}}{v_{E,1}} \frac{\sum v_{A,k} \dot{\xi}_k}{\dot{n}_{E,in}} = \frac{1}{1} \left(\frac{\dot{\xi}_1 - \dot{\xi}_2}{\dot{n}_{E,in}} \right) = \left(\frac{29.3 - 4.3}{70} \right) = 0.36$$

P4.16

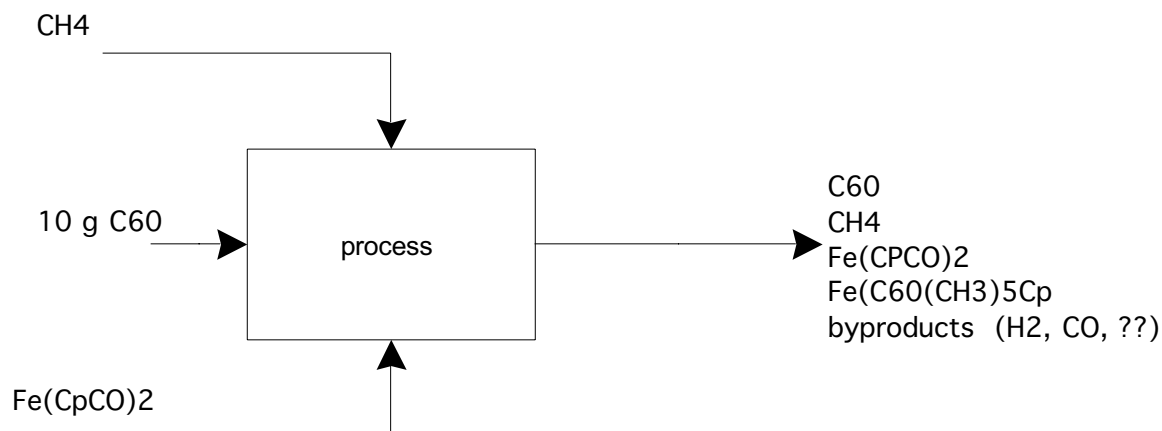
The methylation reaction is



If the reaction to produce the bucky ferrocene occurs without oxygen, hydrogen, or water present, we might guess that the reaction is:



The entire process can be diagrammed as:



The moles of C₆₀ fed to the process is calculated at $\frac{10 \text{ g } C_{60}}{720 \text{ g/gmol}} = 0.0139 \text{ gmol}$. The yield in the first reaction is 95%, or $0.95 \times 0.0139 \text{ gmol} = 0.0132 \text{ gmol}$ C₆₀ are converted to C₆₀(CH₃)₅. Since the ratio of the stoichiometric coefficients equals 1, there are 0.0132 gmol C₆₀(CH₃)₅ generated.

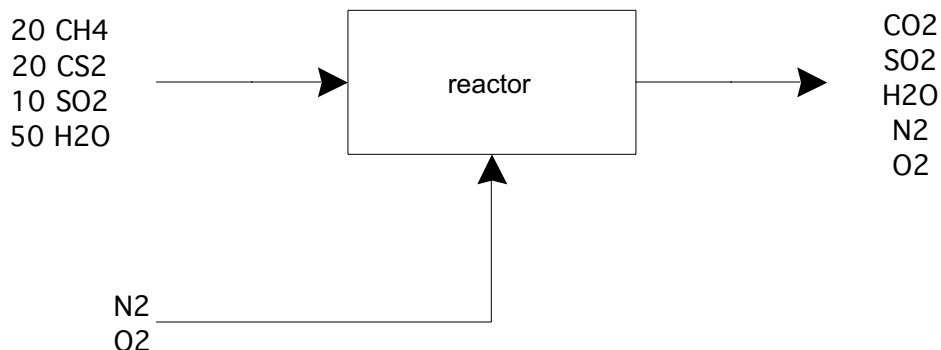
In turn, this product reacts to produce the bucky ferrocene in 52% yield. Assuming that the yield calculation is based on C₆₀(CH₃)₅, then given the stoichiometry of (R2), $0.52 \times 0.0132 = 0.0069$

gmol of $\text{Fe}(\text{C}_{60}(\text{CH}_3)_5)\text{Cp}$ must be generated. The molar mass of this compound is 916 g/gmol, therefore,

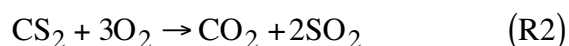
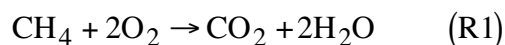
$$0.0069 \text{ gmol Fe}(\text{C}_{60}(\text{CH}_3)_5)\text{Cp} \times 916 \text{ g/gmol} = 6.3 \text{ g Fe}(\text{C}_{60}(\text{CH}_3)_5)\text{Cp}$$

P4.17

No basis is provided, so we'll use 100 gmol/min as a convenient basis. The flow diagram is



Also, we know that the N_2/O_2 ratio in the air feed stream is 79/21. We could solve this problem either by choosing elements (C, S, H, O, N) or compounds as components. We'll solve it here using compounds, which means that we need to write the balanced chemical equations. There are only two (SO_2 and H_2O are already oxidized):



From steady-state material balance equations for methane and carbon disulfide, we find the extents of reaction:

$$\dot{n}_{\text{CH}_4, \text{out}} = 20 - \dot{\xi}_1 = 0$$

$$\dot{\xi}_1 = 20$$

$$\dot{n}_{\text{CS}_2, \text{out}} = 20 - \dot{\xi}_2 = 0$$

$$\dot{\xi}_2 = 20$$

Now we use these numbers to solve the remaining material balances:

$$\dot{n}_{CO_2,out} = \dot{\xi}_1 + \dot{\xi}_2 = 40$$

$$\dot{n}_{SO_2,out} = 10 + 2\dot{\xi}_2 = 50$$

$$\dot{n}_{H_2O,out} = 50 + 2\dot{\xi}_1 = 90$$

$$\dot{n}_{N_2,out} = \dot{n}_{N_2,in}$$

$$\dot{n}_{O_2,out} = \dot{n}_{O_2,in} - 2\dot{\xi}_1 - 3\dot{\xi}_2 = \dot{n}_{O_2,in} - 100$$

We have 2 equations involving 4 unknowns. We use the stream composition specifications to provide the last 2 equations:

$$\frac{\dot{n}_{N_2,in}}{\dot{n}_{O_2,in}} = \frac{79}{21}$$

$$\frac{\dot{n}_{SO_2,out}}{\dot{n}_{SO_2,out} + \dot{n}_{CO_2,out} + \dot{n}_{N_2,out} + \dot{n}_{O_2,out}} = 0.02 = \frac{50}{50 + 40 + \dot{n}_{N_2,out} + \dot{n}_{O_2,out}}$$

(Note: mole fraction SO_2 in outlet is on a dry basis, so water is not included in the denominator.)

We find the solution by substitution or by using an equation solver:

$$\dot{n}_{O_2,in} = 527$$

$$\dot{n}_{O_2,out} = 427$$

$$\dot{n}_{N_2,out} = \dot{n}_{N_2,in} = 1983$$

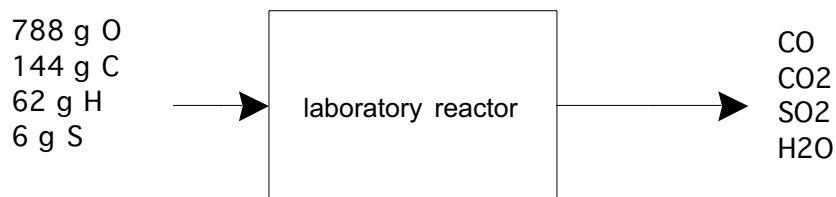
The % excess oxygen is calculated from the amount of oxygen fed that is in excess of stoichiometric requirements, considering both reactions:

$$\frac{\dot{n}_{O_2,in} - (2\dot{\xi}_1 + 3\dot{\xi}_2)}{2\dot{\xi}_1 + 3\dot{\xi}_2} \times 100\% = \frac{527 - 100}{100} \times 100\% = 427\%$$

or, rounding up just to be safe, minimum oxygen excess required is 430%.

The composition of the combustion gases is calculated from the solution of the material balances, knowing that the total outlet flow (at the chosen basis) is $40+50+90+1983+427 = 2590$ gmol/min:

76.6 mol% N_2 , 16.5 mol% O_2 , 1.9 mol% SO_2 , 3.5 mol% H_2O , 1.5 mol% CO_2 .

P4.18

We know the elemental composition of the spent grains, but not the chemical formula of the compounds in the grains, so it is appropriate to use element balances to calculate the exit gas composition and quantity.

First we convert the feed from mass to mole units:

$$\frac{788 \text{ g O}}{16 \text{ g/gmol}} = 49.25 \text{ gmol O}$$

$$\frac{144 \text{ g C}}{12 \text{ g/gmol}} = 12 \text{ gmol C}$$

$$\frac{62 \text{ g H}}{1 \text{ g/gmol}} = 62 \text{ gmol H}$$

$$\frac{6 \text{ g S}}{32 \text{ g/gmol}} = 0.1875 \text{ gmol S}$$

The material balance is simply (in words) IN = OUT for all 4 elements. We'll start with elements that appear in only one compound in the exit gas:

$$\begin{aligned} n_{H,in} = 62 &= 2n_{H_2O,out}, & n_{H_2O,out} &= 31 \text{ gmol} \\ n_{S,in} = 0.1875 &= n_{SO_2,out}, & n_{SO_2,out} &= 0.1875 \text{ gmol} \end{aligned}$$

Now we write the remaining material balance equations:

$$\begin{aligned} n_{C,in} = 12 &= n_{CO,out} + n_{CO_2,out} \\ n_{O,in} = 49.25 &= n_{CO,out} + 2n_{CO_2,out} + 2n_{SO_2,out} + n_{H_2O,out} = n_{CO,out} + 2n_{CO_2,out} + 31.375 \end{aligned}$$

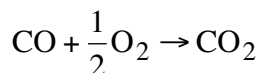
We solve 2 equations in 2 unknowns to find:

$$\begin{aligned} n_{CO,out} &= 6.125 \text{ gmol} \\ n_{CO_2,out} &= 5.875 \text{ gmol} \end{aligned}$$

Total moles of gas produced = 31 + 0.1875 + 6.125 + 5.875 = 43.1875 gmol. The gas composition is 71.8 mol% H₂O, 13.6 mol% CO₂, 14.2 mol% CO and 0.4 mol% SO₂. The standard cubic feet of gas produced is

$$43.1875 \text{ gmol} \times \frac{22.414 \text{ L}}{\text{gmol}} \times \frac{0.353 \text{ ft}^3}{\text{L}} = 34.2 \text{ SCF}$$

Additional oxygen is required just to convert the CO to CO₂. The balanced reaction is



Since there are 6.125 gmol CO produced per kg grain burned in the absence of O₂, we calculate that 0.5 * 6.125 or 3.06 gmol O₂ is required for complete combustion. Since air is 21 mol% O₂, this is equivalent to 11.5 gmoles air per kg grain.

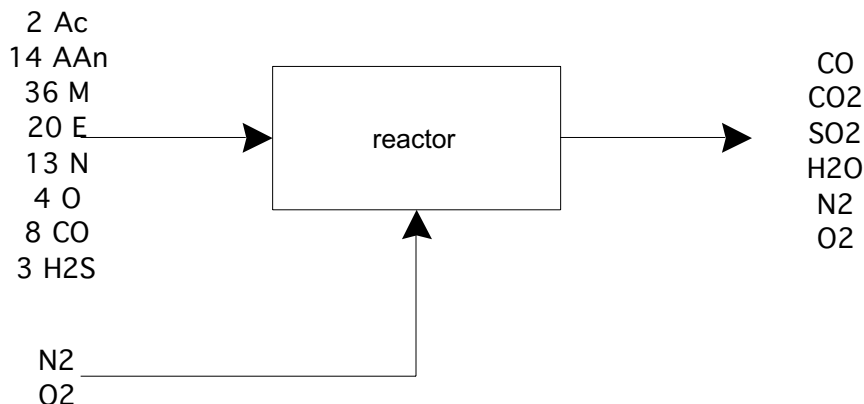
Now, we'll repeat the calculations but assume that there is 14.6 gmoles air fed (3.06 gmol O₂, 11.5 gmol N₂) along with the 1 kg grain. The reactor product gases are: 12 moles CO₂, 11.5 moles N₂, 0.1875 gmol SO₂, and 31 gmol H₂O. Total gmoles = 54.7 gmol, so the percentage of SO₂ in the exit gas is

$$\frac{0.1875}{54.7} \times 100\% = 0.34 \text{ mol\% SO}_2$$

This is lower than the maximum allowable SO₂ limits. Given that the grains are free, it seems like a good idea to accept the donation.

P4.19

Assuming a convenient basis of 100 gmol/min fed, the flow diagram becomes:



There are 13 compounds but only 5 elements, so an element balance approach is attractive.

C balance:

$$2(3) + 14(4) + 36(1) + 20(2) + 8(1) = 146 = \dot{n}_{\text{CO}_2, \text{out}} + \dot{n}_{\text{CO}, \text{out}}$$

H balance:

$$2(6) + 14(6) + 36(4) + 20(6) + 3(2) = 366 = 2\dot{n}_{\text{H}_2\text{O}, \text{out}}$$

$$\dot{n}_{\text{H}_2\text{O}, \text{out}} = 183$$

S balance:

$$3(1) = 3 = \dot{n}_{SO_2,out}$$

$$\dot{n}_{SO_2,out} = 3$$

O balance:

$$2(1) + 14(3) + 4(2) + 8(1) + 2\dot{n}_{O_2,in} = 2\dot{n}_{O_2,out} + 183 + 3(2) + \dot{n}_{CO,out} + 2\dot{n}_{CO_2,out}$$

$$2\dot{n}_{O_2,in} = 2\dot{n}_{O_2,out} + \dot{n}_{CO,out} + 2\dot{n}_{CO_2,out} + 129$$

N balance:

$$13(2) + 2\dot{n}_{N_2,in} = 2\dot{n}_{N_2,out}$$

$$2\dot{n}_{N_2,in} = 2\dot{n}_{N_2,out} - 26$$

We still have 6 unknowns, but we have not yet used all our specifications. First, we know the composition of the inlet air, or

$$\frac{\dot{n}_{O_2,in}}{\dot{n}_{N_2,in}} = \frac{21}{79}$$

We also know that oxygen is fed at 20% excess, calculated on the assumption of complete combustion. We can use our element balance equations to first solve the case of complete combustion with a stoichiometric oxygen feed rate, where there is no CO and no O₂ in the effluent. This allows us to find the oxygen (and nitrogen) feed rate at 0% excess, thereby allowing us to calculate the oxygen feed rate at 20% excess. Then we use the calculated air feed rate and the specification on the actual CO:CO₂ ratio to find the actual burner outlet.

Complete combustion case: solve equations above for $\dot{n}_{CO,out} = 0$ and $\dot{n}_{O_2,out} = 0$:

$$\dot{n}_{CO_2,out} = 146$$

$$\dot{n}_{O_2,in} = \frac{2(146) + 129}{2} = 210.5$$

$$\dot{n}_{N_2,in} = \frac{79}{21}(210.5) = 792$$

Actual case: At 20% excess, the oxygen in is 1.2(210.5) or 252.6 gmol/min (at the chosen basis) and the nitrogen in is 1.2(792)=950.4.

Also, we know that $\frac{\dot{m}_{CO_2,out}}{\dot{m}_{CO,out}} = \frac{4}{1}$. This is a mass ratio, but we are working in moles, so we need the molar masses to convert to a mole ratio:

$$\frac{\dot{n}_{CO_2,out}}{\dot{n}_{CO,out}} = \frac{\dot{m}_{CO_2,out}}{\dot{m}_{CO,out}} \frac{M_{CO}}{M_{CO_2}} = \frac{4}{1} \left(\frac{28}{44} \right) = 2.55$$

Going back to our element balance equations with these changes and solving, we find:

$$\dot{n}_{N_2,out} = 963$$

$$\dot{n}_{CO_2,out} = 104.9$$

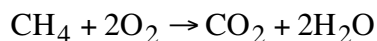
$$\dot{n}_{CO,out} = 41.4$$

$$\dot{n}_{O_2,out} = 62.65$$

The total flow out of the burner is $183+3+963+104.9+41.4+62.65=1358$, so the burner outlet composition is: 4.6 mol% O₂, 70.9 mol% N₂, 3.0 mol% CO, 7.7 mol% CO₂, 13.5 mol% H₂O, 0.22 mol% SO₂.

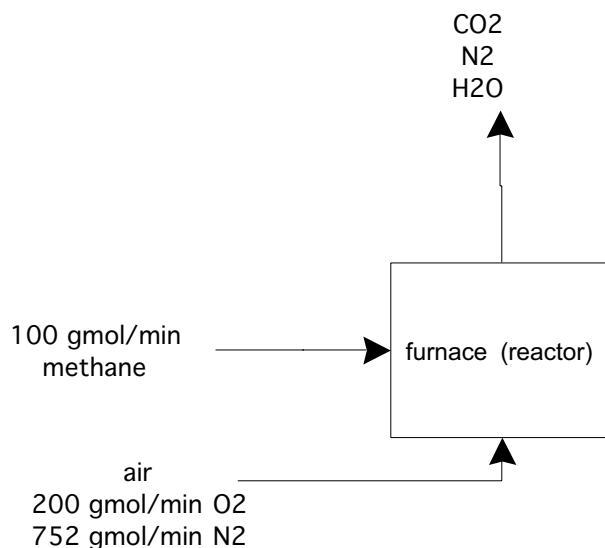
P4.20

We'll assume that natural gas is 100% methane (CH₄). (Alternatively, calculations could be completed using the natural gas composition given in Example 4.2.) Complete combustion of methane is described by the chemical reaction:



We'll also assume that the air is supplied at its stoichiometric ratio. (Home furnaces operate with some excess air, to avoid CO formation. But any excess air would reduce the CO₂ content of the flue gases, so we will be calculating the maximum possible CO₂ content with the assumption of stoichiometric feed ratio of air:methane.)

We'll choose 100 gmol/min methane fed to the furnace as a convenient basis.



Assuming steady-state operation, the material balance equations are:

$$\dot{n}_{N_2,out} = \dot{n}_{N_2,in} = 752 \text{ gmol/min}$$

$$\dot{n}_{CH_4,out} = 0 = \dot{n}_{CH_4,in} + \nu_{CH_4} \dot{\xi} = 100 - \dot{\xi}, \quad \dot{\xi} = 100 \text{ gmol/min}$$

$$\dot{n}_{CO_2,out} = v_{CO_2} \dot{\xi} = 1 \times 100 = 100 \text{ gmol/min}$$

$$\dot{n}_{H_2O,out} = v_{H_2O} \dot{\xi} = 2 \times 100 = 200 \text{ gmol/min}$$

On a dry basis (excluding water), the mol% CO₂ is

$$\frac{100}{100 + 752} \times 100\% = 11.7 \text{ mol\%}$$

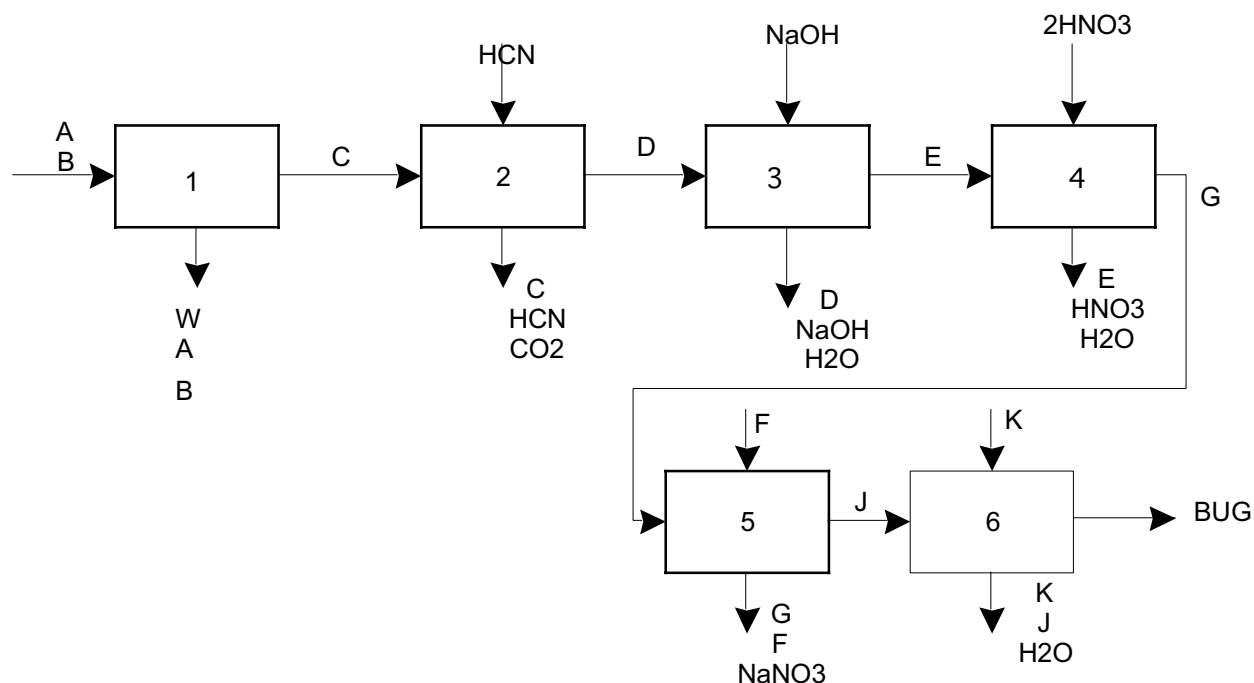
The wt% CO₂ is

$$\frac{100(44)}{100(44) + 752(28)} \times 100\% = 17.3 \text{ wt\%}$$

Neither number is even close to the handyman's claim of 30% CO₂. The handyman is not so handy!

P4.21

The flow diagram, in which we've lumped together mixers, reactors and separators for each reaction, is:



This is an example of a diverging tree (see Chapter 3). It is easiest to start at the beginning and work through the process, then scale up to the final desired BUG production rate. Starting with 100 kgmol A fed as a basis, and assuming stoichiometric feed of all components, we work through the calculations as:

Compound	1		2		3		4		5		6	
	in	out	in	out	in	out	in	out	in	out	in	out
A	100	8										
B	100	8										
C		92	92	14.7								
D				77.3	77.3	2.3						
E						75	75	3.75				
F									142.5	4.3		
G								71.25	71.25	2.14		
J										69.1	69.1	0.7
K											69.1	0.7
H ₂ O		8				150		71.25				136.8
HCN			92	14.7								
CO ₂				77.3								
NaOH					154.6	4.6						

HNO ₃							150	7.5				
NaNO ₃										138.2		
BUG												68.4

We've made 68.4 moles BUG, plus a number of waste streams. To scale up to 100 kgmol, multiply everything by 100/68.4 or 1.46.

Raw materials fed (kgmol):

A	146
B	146
F	208
K	101
HCN	135
NaOH	226
HNO ₃	219
Total	1180

Waste products:

A	11.7
B	11.7
C	21.5
D	3.4
E	5.5
F	6.3
G	3.1
J	1.0
K	1.0
HCN	21.5
NaOH	6.7
HNO ₃	11
H ₂ O	535
NaNO ₃	202
CO ₂	113
Total	954

Molar ratio of waste products to desired product is 9.54. This could be reduced by recovering and recycling unreacted reactants.

P4.22

	High recycle:purge ratio	Low recycle:purge ratio
Production rate of B	same	same
Fresh feed rate	lower	higher
% A in purge	lower	higher
% I in feed to reactor	higher	lower
Reactor volume required	higher	lower
Equipment costs	higher	lower
Raw material costs	lower	higher

P4.23

From the problem statement, we know that

$$m_{b,sys,f} = 500 \text{ g} = m_{b,sys,0} \exp(0.17t_f) = 20 \exp(0.17t_f)$$

Solving, we find the length of time that the fermentation runs:

$$t_f = 18.9 \text{ h.}$$

To find the total amount of insulin, we use an integral material balance on insulin. Since the fermentation is a batch process, no insulin enters or leaves the vessel over the course of the fermentation, therefore the material balance equation for insulin reduces to:

$$m_{ins,sys,f} - m_{ins,sys,0} = \int_0^{18.9} \dot{R}_{ins} dt = \int_0^{18.9} 16m_{b,sys} dt = \int_0^{18.9} 16m_{b,sys,0} \exp(0.17t) dt$$

Given that there is no insulin in the fermentor initially, we integrate to find

$$m_{ins,sys,f} = \frac{16(20)}{0.17} [\exp(0.17(18.9)) - \exp(0)] = 44,900 \text{ mg insulin.}$$

P4.24

Choose as a basis 1000 gmol of reactant A and a reaction described as



For the conventional process,

$$y_{A \rightarrow P} = 0.54 = \frac{\int_0^{48h} \dot{\xi} dt}{1000}, \text{ or } \dot{\xi} = 11.25 \text{ gmol/h}$$

For the microwave process,

$$y_{A \rightarrow P} = 0.90 = \frac{\int_0^{0.0667h} \dot{\xi} dt}{1000}, \text{ or } \dot{\xi} = 13,500 \text{ gmol/h}$$

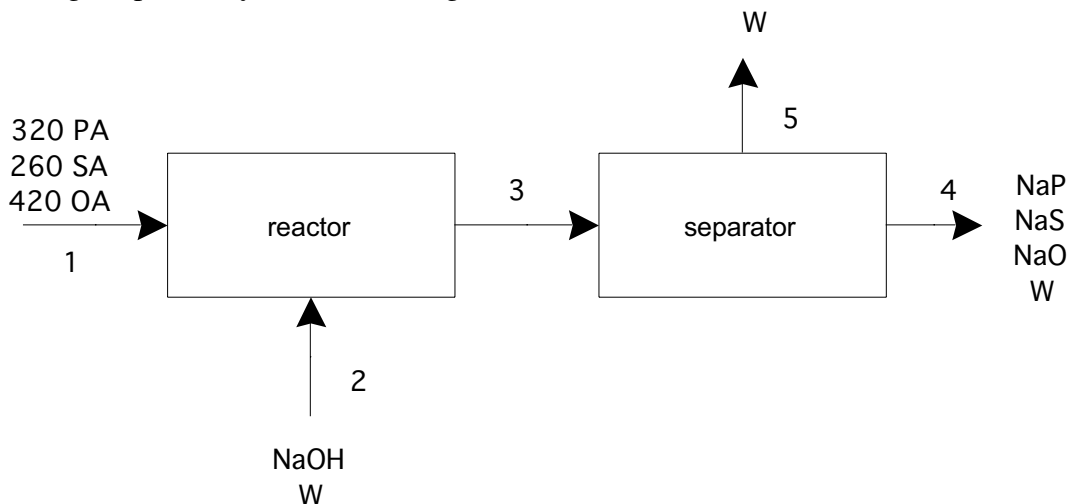
The percentage increase in reaction rate for the microwave over the conventional process is

$$\frac{13,500 - 11.25}{11.25} \times 100\% = 119,900\% \text{ (or about 1200-fold increase!)}$$

The reaction stoichiometry assumed does not matter in calculating the relative increase in reaction rate.

P4.25

We'll choose one metric ton fatty acids (1000 kg) per day fed to the process as a convenient basis to begin calculations, then scale up or down later. (It is also possible to solve this problem using 1000 kg soap directly.) The flow diagram with our new basis is:



where PA, SA, and OA are palmitic acid, stearic acid, and oleic acid, and NaP, NaS, and NaO are the corresponding sodium salts.

With a reacting system and reactions of known stoichiometry, it is generally easier to work with moles rather than mass. Since the information given in the problem is in mass units, we need to convert. Molar masses of PA, SA and OA are 256, 284, and 282 g/gmol, respectively. From this we calculate:

$$\dot{n}_{PA,1} = \frac{\dot{m}_{PA,1}}{M_{PA}} = \frac{320}{256} = 1.25 \text{ kgmol/day}$$

$$\dot{n}_{SA,1} = \frac{260}{284} = 0.9155 \text{ kgmol/day}$$

$$\dot{n}_{OA,1} = \frac{420}{282} = 1.49 \text{ kgmol/day}$$

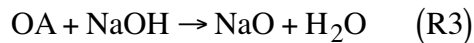
Given that all the fatty acids fed are converted to their sodium salt, we find that

$$\dot{\xi}_1 = 1.25 \text{ kgmol/day}$$

$$\dot{\xi}_2 = 0.9155 \text{ kgmol/day}$$

$$\dot{\xi}_3 = 1.49 \text{ kgmol/day}$$

where



From this reaction stoichiometry and material balances on sodium palmitate, sodium stearate, and sodium oleate, and the known molar masses of NaP, NaS, and NaO, we calculate

$$\dot{m}_{NaP,3} = \dot{m}_{NaP,5} = \dot{n}_{NaP,3} M_{NaP} = 1.25(278) = 347.5 \text{ kg/day}$$

$$\dot{m}_{NaS,3} = \dot{m}_{NaS,5} = \dot{n}_{NaS,3} M_{NaS} = 0.9155(306) = 280 \text{ kg/day}$$

$$\dot{m}_{NaO,3} = \dot{m}_{NaO,5} = \dot{n}_{NaO,3} M_{NaO} = 1.49(304) = 453 \text{ kg/day}$$

No NaOH leaves the reactor, so the material balance equation on NaOH gives us:

$$\dot{n}_{NaOH,3} = 0 = \dot{n}_{NaOH,2} - \dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3$$

$$\dot{n}_{NaOH,2} = 1.25 + 0.9155 + 1.49 = 3.656 \text{ kgmol/day}$$

Multiplying by the molar mass (40) of NaOH gives us a feed rate of 146 kg NaOH/day.

Since NaOH solution is 24 wt% caustic and 76 wt% water,

$$\dot{m}_{W,2} = \left(\frac{76}{24} \right) 146 = 463 \text{ kg/day}$$

A material balance on water around the reactor (with molar mass = 18 kg/kgmol) gives:

$$\dot{m}_{W,3} = 463 + (\dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3)(18) = 529 \text{ kg/day}$$

The final product is 12 wt% water, or

$$\frac{\dot{m}_{W,4}}{\dot{m}_4} = 0.12 = \frac{\dot{m}_{W,4}}{\dot{m}_{W,4} + 347.5 + 280 + 453}$$

$$\dot{m}_{W,4} = 147.3 \text{ kg/day}$$

Water removed in the separator is

$$\dot{m}_{W,5} = 529 - 147.3 = 381.7 \text{ kg/day}$$

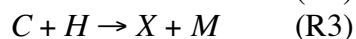
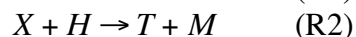
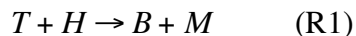
Total soap made with this basis is $347.5 + 280 + 453 + 147.3 = 1228 \text{ kg}$ or 1.228 metric tons. To get to the desired basis of 1000 kg soap, we scale down by $1/1.228$ to find

$$\text{Fatty acid required} = 1000/1.228 = 814 \text{ kg/day}$$

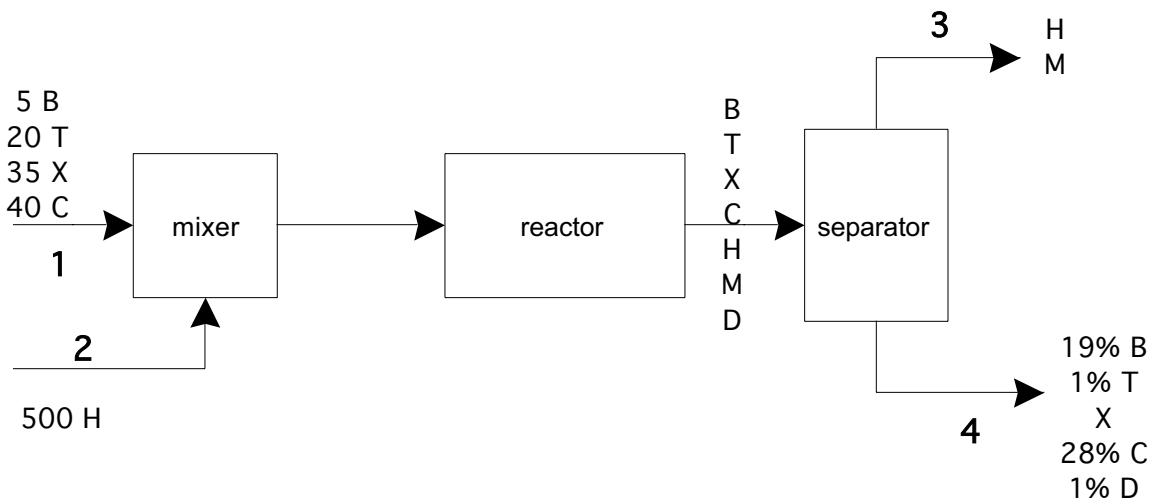
$$\text{Water removed} = 381.7/1.228 = 311 \text{ kg/day}$$

P4.26

There are 7 compounds participating in 4 reactions: toluene (T), hydrogen (H), benzene (B), methane (M), xylene (X), pseudocumene (C) and diphenyl (D). The reactions are written in shorthand as:



The flow diagram, with flows shown as gmol/h, is



If we lump together the mixer, reactor and separator as a single system operating at steady state, we have 4 streams (numbered in the flow diagram). A DOF analysis tells us that there are 12 stream variables plus 4 system (reaction) variables, and there are 2 specified flows, 7 independently specified stream compositions, and 7 material balance equations. Therefore $\text{DOF} = (12 + 4) - (2 + 7 + 7) = 16 - 16 = 0$, and the problem is completely specified.

We start by writing the material balance equations for the aromatic compounds:

$$\begin{aligned}\dot{n}_{B4} &= 5 + \dot{\xi}_1 - 2\dot{\xi}_4 \\ \dot{n}_{T4} &= 20 - \dot{\xi}_1 + \dot{\xi}_2 \\ \dot{n}_{X4} &= 35 - \dot{\xi}_2 + \dot{\xi}_3 \\ \dot{n}_{C4} &= 40 - \dot{\xi}_3 \\ \dot{n}_{D4} &= \dot{\xi}_4\end{aligned}$$

Although not essential, it is convenient to also write a variable for the total molar flow rate in stream 4, obtained by summing up the compound molar flows:

$$\dot{n}_4 = \dot{n}_{B4} + \dot{n}_{T4} + \dot{n}_{X4} + \dot{n}_{C4} + \dot{n}_{D4} = 100 - \dot{\xi}_4$$

The composition of stream 4 is fully specified, providing 4 more independent equations:

$$\begin{aligned}\frac{\dot{n}_{B4}}{\dot{n}_4} &= 0.19 \\ \frac{\dot{n}_{T4}}{\dot{n}_4} &= 0.01 \\ \frac{\dot{n}_{C4}}{\dot{n}_4} &= 0.28 \\ \frac{\dot{n}_{D4}}{\dot{n}_4} &= 0.01\end{aligned}$$

This system of equations is solved by substituting in expressions for the molar flow rates in terms of the 4 reaction variables into the composition equations. It is best to start with D and work backwards (because diphenyl participates in only one reaction). We find:

$$\dot{\xi}_4 = 0.99, \dot{\xi}_3 = 12.3, \dot{\xi}_2 = -3.2, \text{ and } \dot{\xi}_1 = 15.8.$$

(The negative extent of reaction for R3 is an indication that we've written the reaction in the "wrong" direction.)

The fractional conversions of all reactants are now easily calculated:

$$\begin{aligned}f_{CT} &= -\frac{(-1)\dot{\xi}_1 + \dot{\xi}_2}{20} = \frac{15.8 + 3.2}{20} = 0.95 \\ f_{CC} &= -\frac{(-1)\dot{\xi}_3}{40} = \frac{12.3}{40} = 0.3075\end{aligned}$$

(Benzene and xylene are net *products* of the reaction network; even though they are both in the feed to the reactor, so we do not calculate fractional conversions.)

$$f_{CH} = -\frac{(-1)\dot{\xi}_1 + (-1)\dot{\xi}_2 + (-1)\dot{\xi}_3 + \dot{\xi}_4}{500} = \frac{15.8 - 3.2 + 12.3 - 0.99}{500} = 0.0048$$

The methane and hydrogen flows are calculated from material balance equations:

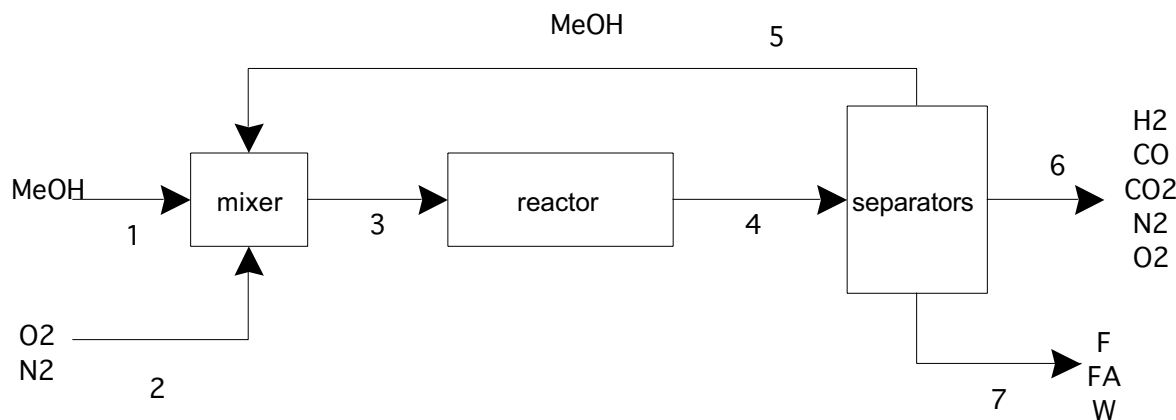
$$\begin{aligned}\dot{n}_{M3} &= \dot{\xi}_1 + \dot{\xi}_2 + \dot{\xi}_3 = 24.9 \text{ gmol/h} \\ \dot{n}_{H3} &= 500 - \dot{\xi}_1 - \dot{\xi}_2 - \dot{\xi}_3 + 0.99 = 476 \text{ gmol/h}\end{aligned}$$

The mol% methane in stream 3 is

$$\frac{24.9}{24.9 + 476} \times 100\% = 4.97 \text{ mol\%}$$

P4.27

The flow diagram is shown, with MeOH = methanol, F = formaldehyde, FA = formic acid, W = water, and streams numbered.



We need to choose a basis: 100 gmoles/min MeOH feed to the reactor (stream 3) is one convenient basis (there are other possible choices – such as the offgas flowrate.) From the stream composition specification for stream 3 we find:

$$0.35 = \frac{\dot{n}_{MeOH,3}}{\dot{n}_{MeOH,3} + \dot{n}_{O2,3} + \dot{n}_{N2,3}} = \frac{100}{100 + \dot{n}_{O2,3} + \dot{n}_{N2,3}}$$

We also know that air is 79 mol% N₂, 21 mol% O₂, and a balance around the mixer tells us that this ratio is preserved in the feed to the reactor, or

$$\frac{\dot{n}_{O2,3}}{\dot{n}_{N2,3}} = \frac{21}{79}$$

We readily solve these two equations in two unknowns to find:

$$\begin{aligned}\dot{n}_{O2,3} &= 39 \\ \dot{n}_{N2,3} &= 146.7\end{aligned}$$

The nitrogen balance around the reactor and separator tell us

$$\dot{n}_{N2,3} = \dot{n}_{N2,4} = \dot{n}_{N2,6} = 146.7$$

Since the off gas stream (stream 6) is 74.5 mol% N₂, we can find the total offgas flow rate and then, since we know the mol% of all other compounds in this stream we can also find their flow rates. These calculations yield the following:

$$\begin{aligned}\dot{n}_{H2,6} &= \dot{n}_{H2,4} = 39.8 \\ \dot{n}_{CO2,6} &= \dot{n}_{CO2,4} = 9.45 \\ \dot{n}_{CO,6} &= \dot{n}_{CO,4} = 0.394 \\ \dot{n}_{O2,6} &= \dot{n}_{O2,4} = 0.594\end{aligned}$$

We also know the fractional conversion of methanol in the reactor is 0.8, so we readily calculate that

$$\dot{n}_{MeOH,4} = 100 - 0.8(100) = 20$$

Now we are ready to attack the material balance equation on the reactor. The problem can be solved either (a) by using compounds as components, determining a set of independent chemical reactions, and balancing those reaction or (b) by using elements as components. We'll use approach (b), because then we don't have to work out all the reaction stoichiometry.

C balance:

$$100 = 20 + 9.45 + 0.394 + \dot{n}_{F,4} + \dot{n}_{FA,4}$$

$$\dot{n}_{F,4} + \dot{n}_{FA,4} = 70.156$$

H balance:

$$400 = 20(4) + 39.8(2) + 2\dot{n}_{W,4} + 2\dot{n}_{F,4} + 2\dot{n}_{FA,4} = 159.6 + 2\dot{n}_{W,4} + 2\dot{n}_{F,4} + 2\dot{n}_{FA,4}$$

$$\dot{n}_{W,4} + \dot{n}_{F,4} + \dot{n}_{FA,4} = 120.2$$

O balance:

$$100 + 39(2) = 20 + 9.45(2) + 0.394 + 0.594(2) + \dot{n}_{W,4} + \dot{n}_{F,4} + 2\dot{n}_{FA,4}$$

$$\dot{n}_{W,4} + \dot{n}_{F,4} + 2\dot{n}_{FA,4} = 137.52$$

(The N balance has already been solved.) We have 3 equations in 3 unknowns, which can be solved simultaneously to find:

$$\dot{n}_{W,4} = \dot{n}_{W,7} = 50$$

$$\dot{n}_{F,4} = \dot{n}_{F,7} = 52.9$$

$$\dot{n}_{FA,4} = \dot{n}_{FA,7} = 17.3$$

The fresh methanol feed rate is obtained from a balance around the mixer to be 80 gmol/min. Therefore, the moles of formaldehyde produced per mole of fresh methanol feed is 52.9/80 or 0.66 moles/mole.

P4.28

Methanol is the limiting reactant, because $\frac{3000}{200} = 15 > \frac{\nu_i}{\nu_M} = 6$, where i is either NaClO_3 or H_2SO_4 and M indicates methanol. The fractional conversion of methanol is 0.9, or

$$f_{CM} = 0.9 = \frac{200 - \dot{n}_{M,out}}{200} = \frac{\dot{\xi}}{200}, \quad \text{so } \dot{\xi} = 180 \text{ kgmol/h}$$

Therefore:

$$\dot{n}_{M,out} = 20 \text{ kgmol/h}$$

From the material balance equation we calculate the remaining components:

$$\dot{n}_{\text{H}_2\text{SO}_4,out} = 3000 - 6(180) = 1920 \text{ kgmol/h}$$

$$\dot{n}_{\text{NaClO}_3,out} = 3000 - 6(180) = 1920 \text{ kgmol/h}$$

$$\dot{n}_{\text{ClO}_2,out} = 6(180) = 1080 \text{ kgmol/h}$$

$$\dot{n}_{\text{NaHSO}_4,out} = 6(180) = 1080 \text{ kgmol/h}$$

$$\dot{n}_{\text{CO}_2,out} = 180 \text{ kgmol/h}$$

$$\dot{n}_{\text{H}_2\text{O},out} = 5(180) = 900 \text{ kgmol/h}$$

The total molar flow out of the reactor = $20 + 1920 + 1920 + 1080 + 1080 + 180 + 900 = 7100$ kgmol/h. The composition is 0.3 mol% CH_3OH , 27 mol% each H_2SO_4 and NaClO_3 , 15.2 mol% each ClO_2 and NaHSO_4 , 2.5 mol% CO_2 , and 12.7 mol% H_2O .

P4.29

We'll model the gases using the ideal gas law. At STP, an ideal gas is 22.4 L/gmol.

$$\text{The inlet gas is } \frac{51.38 \text{ cm}^3}{\text{min}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{1 \text{ mol}}{22.4 \text{ L}} \times \frac{1000 \text{ mmol}}{\text{mol}} = \frac{2.294 \text{ mmol}}{\text{min}}$$

$$\begin{aligned}\text{Propane: } & 0.00086 \times \frac{2.294 \text{ mmol}}{\text{min}} = \frac{0.00197 \text{ mmol}}{\text{min}} \\ \text{Isobutane: } & 0.329 \times \frac{2.294 \text{ mmol}}{\text{min}} = \frac{0.755 \text{ mmol}}{\text{min}} \\ \text{n-butane: } & 0.00068 \times \frac{2.294 \text{ mmol}}{\text{min}} = \frac{0.00156 \text{ mmol}}{\text{min}} \\ \text{hydrogen: } & 0.669 \times \frac{2.294 \text{ mmol}}{\text{min}} = \frac{1.535 \text{ mmol}}{\text{min}}\end{aligned}$$

Similar calculations give us that the outlet gas flow rate is 2.705 mmol/min, and the flows of the individual components are:

Methane:	0.0095 mmol./min
Ethane:	0.0010 mmol/min
Propane:	0.00092 mmol/min
Isobutane:	0.365 mmol/min
n-butane:	0.0054 mmol/min
isobutylene:	0.373 mmol/min
cis-butene:	0.0010 mmol/min
trans-butene:	0.0012 mmol/min
Hydrogen:	1.937 mmol/min

We will check reliability of data by elemental balances: does $In = Out$?

C balance:

$$\begin{aligned}In &= 3(0.00197) + 4(0.755) + 4(0.00156) = 3.032 \text{ mmol/min C} \\ Out &= 0.0095 + 2(0.001) + 3(0.00092) + 4(0.365 + 0.0054 + 0.0010 + 0.0012) = 2.996 \text{ mmol/min C}\end{aligned}$$

$$3.032 \text{ mmol/min} = 2.996 \text{ mmol/min} ? \text{ Close enough!}$$

H balance:

$$\begin{aligned}In &= 8(0.00197) + 10(0.755 + 0.00156) + 2(1.535) = 10.65 \text{ mmol/min H} \\ Out &= 4(0.0095) + 6(0.001) + 8(0.00092 + 0.0010 + 0.373 + 0.0012) \\ &\quad + 10(0.365 + 0.0054) + 2(1.937) = 10.63 \text{ mmol/min H} \\ 10.65 \text{ mmol/min} &= 10.63 \text{ mmol/min} ? \text{ Close enough!}\end{aligned}$$

These are both remarkably close for experimental data.

The fractional conversion of isobutane is calculated from the data as:

$$f_{C,iB} = \frac{\dot{n}_{iB,in} - \dot{n}_{iB,out}}{\dot{n}_{iB,in}} = \frac{0.755 - 0.365}{0.755} = 0.517$$

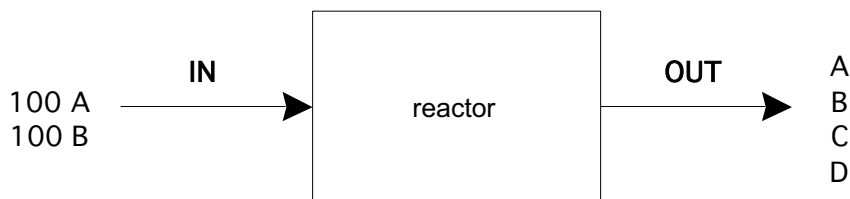
The selectivity is the moles of isobutylene (iBe) produced per mole of isobutane reacted

$$s_{iB \rightarrow iBe} = \frac{\dot{n}_{iBe,out}}{\dot{n}_{iB,in} - \dot{n}_{iB,out}} = \frac{0.373}{0.755 - 0.365} = 0.956$$

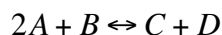
The yield (0.517×0.956 , or 0.494) is much lower than 100% because almost half of the isobutene is unreacted. The selectivity is below 100%, most likely because some of the isobutane is converted to isomers of isobutylene: cis and trans butene. There is also some conversion to n-butane.

P4.30

Imagining a flow diagram, with the reactor outlet at equilibrium, we have:



The reaction is



Since this is a gas-phase reaction, we say that

$$K_a = \frac{(y_C P)(y_D P)}{(y_A P)^2 (y_B P)} = \frac{y_C y_D}{y_A^2 y_B} \frac{1}{P}$$

The mole fractions of each are related to the moles of each component and the total moles, as well as the extent of reaction at equilibrium:

	$\dot{n}_{i,out} = \dot{n}_{i,in} + \nu_i \dot{\xi}$	Mole fraction $y_i = \frac{\dot{n}_{i,out}}{\dot{n}_{out}}$
A	$100 - 2\dot{\xi}$	$\frac{100 - 2\dot{\xi}}{200 - \dot{\xi}}$
B	$100 - \dot{\xi}$	$\frac{100 - \dot{\xi}}{200 - \dot{\xi}}$
C	$\dot{\xi}$	$\frac{\dot{\xi}}{200 - \dot{\xi}}$
D	$\dot{\xi}$	$\frac{\dot{\xi}}{200 - \dot{\xi}}$
total	$200 - \dot{\xi}$	1

Substituting in the expressions for mole fraction into the K_a equation and simplifying, we find:

$$K_a = \frac{\xi^2(200 - \xi)}{(100 - 2\xi)^2(100 - \xi)} \frac{1}{P}$$

K_a is a constant. If P increases, then $\frac{1}{P}$ decreases, and $\frac{\xi^2(200 - \xi)}{(100 - 2\xi)^2(100 - \xi)}$ must increase to

keep K_a constant. This happens if ξ increases. (You can check this by plugging in two different values for ξ and calculating this term. The maximum value of ξ is 50.) Thus, increasing P will increase fractional conversion of A.

P4.31

For glucose metabolism (assuming liquid water)

$$\Delta \hat{G}_r^\circ = \sum v_i \Delta \hat{G}_{f,i}^\circ = (-1)(-910.56) + 6(-394.37) + 6(-237.19) = -2879 \text{ kJ/gmol}$$

(The Gibbs energy of formation for glucose is available in references such as Lange's Handbook of Chemistry.)

There is synthesis of 6 moles of ATP from ADP per mol of oxygen consumed, and since there are 6 moles oxygen consumed per mole glucose consumed, there are 36 moles ATP generated per mole glucose consumed, or

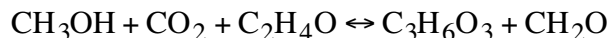
$$\Delta \hat{G}_r^\circ = \sum v_i \Delta \hat{G}_{f,i}^\circ = \frac{36 \text{ gmol ATP}}{\text{gmol glucose}} \left(\frac{-7.3 \text{ kcal}}{\text{gmol ATP}} \right) \left(\frac{4.184 \text{ kJ}}{\text{kcal}} \right) = -1100 \text{ kJ/gmol}$$

Conversion efficiency is $\frac{1100}{2879} \times 100\% = 38\%$

P4.32

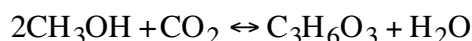
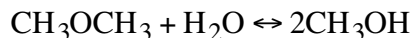
Scheme 1:

The balanced chemical reaction is



Scheme 2:

The balanced chemical reactions are



or, the net reaction is:



First we will collect molar mass, cost, and energy data to assist with evaluating these two schemes. Prices are from the table on p. 312, or from *Chemical Market Reporter*. Gibbs energy of formation and enthalpy of formation are from Table B.3 (all assumed gas phase).

Compound	Molar mass, g/gmol	$\Delta\hat{G}_f^\circ$, kJ/gmol	$\Delta\hat{H}_f^\circ$, kJ/gmol	\$/kg
CH ₃ OH	32	-162.32	-200.94	0.188
CO ₂	44	-394.37	-393.5	negligible
C ₂ H ₄ O	44	-13.23	-52.63	1.00
CH ₂ O	30	-102.6	-108.6	0.46
CH ₃ OCH ₃	46	-109.0	-184.1	~1.00 (estimate)
C ₃ H ₆ O ₃	90	-452.4	-570.1	3.11

Atom economy analysis:

$$\text{Scheme 1, fractional atom utilization} = \frac{90}{32 + 44 + 44} = 0.75 \text{ (not bad, not great)}$$

Byproduct is formaldehyde, there is a market for that product.

$$\text{Scheme 2, fractional atom utilization} = \frac{90}{46 + 44} = 1.0 \text{ (awesome!)}$$

Both schemes are quite competitive on an atom economy basis with the schemes analyzed in Example 4.16.

Process economy analysis:

Scheme 1,

Compound	Moles	Molar mass, g/gmol	mass	kg (SF = 100/90)	\$/kg	\$
CH ₃ OH	-1	32	-32	-35.5	0.188	-6.67
CO ₂	-1	44	-44	-48.9	negligible	0
C ₂ H ₄ O	-1	44	-44	-48.9	1.00	-48.9
CH ₂ O	+1	30	+30	+33.3	0.46	+15.3
C ₃ H ₆ O ₃	+1	90	+90	+100	3.11	+311
net						+270.73

This process makes a lot of money - \$2.70/kg DMC. Raw material costs are \$0.56/kg DMC, which is higher but still reasonable compared to schemes R2, R3, and R4 in the example problem.

Scheme 2,

Compound	Moles	Molar mass,	mass	kg (SF = 100/90)	\$/kg	\$
----------	-------	----------------	------	---------------------	-------	----

		g/gmol				
CH ₃ OCH ₃	-1	46	-46	-51.1	~1.00	-51.1
CO ₂	-1	44	-44	-48.9	negligible	0
C ₃ H ₆ O ₃	+1	90	+90	+100	3.11	+311
net						+260

The process economics for Scheme 2 are pretty similar to Scheme 1.

Chemical reaction equilibrium analysis:

Scheme 1,

$$\Delta \hat{G}_r = 162.32 + 394.37 + 13.23 - 102.6 - 452.4 = 14.9 \text{ kJ/gmol}$$

$$\Delta \hat{H}_r = 200.94 + 393.5 + 52.63 - 108.6 - 570.1 = -31.6 \text{ kJ/gmol}$$

$$\ln K_a = -\frac{1}{8.3144} \left[\frac{14,900 + 31600}{298} - \frac{31600}{T} \right] = -18.77 + \frac{3800}{T}$$

$$K_a(100^\circ\text{C}) = \exp\left(-18.77 + \frac{3800}{373}\right) = 0.000187$$

$$K_a(500^\circ\text{C}) = \exp\left(-18.77 + \frac{3800}{773}\right) = 9.6 \times 10^{-7}$$

Not an attractive equilibrium!

Scheme 1,

$$\Delta \hat{G}_r = 109.0 + 394.37 - 452.4 = +50.97 \text{ kJ/gmol}$$

$$\Delta \hat{H}_r = 184.1 + 393.5 - 570.1 = +7.5 \text{ kJ/gmol}$$

$$\ln K_a = -\frac{1}{8.3144} \left[\frac{50970 - 7500}{298} - \frac{7500}{T} \right] = -168 + \frac{900}{T}$$

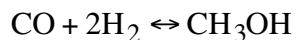
$$K_a(100^\circ\text{C}) = \exp\left(-168 + \frac{900}{373}\right) = 10^{-72}$$

$$K_a(500^\circ\text{C}) = \exp\left(-168 + \frac{900}{773}\right) = 3 \times 10^{-73}$$

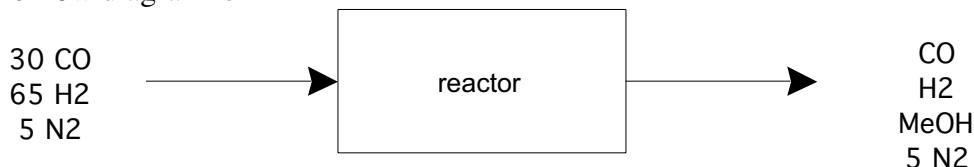
Very unfavorable equilibrium!.

P4.33

The balanced chemical equation is



The flow diagram is



with the reactor outlet stream assumed at equilibrium. The material balance equations are

$$\dot{n}_{\text{CO},out} = 30 - \dot{\xi}$$

$$\dot{n}_{\text{H}_2,out} = 65 - 2\dot{\xi}$$

$$\dot{n}_{\text{MeOH},out} = \dot{\xi}$$

$$\dot{n}_{\text{N}_2,out} = 5$$

$$\dot{n}_{out} = 100 - 2\dot{\xi}$$

(with all flows in kmol/h.) The equilibrium constant for this gas-phase reaction, written in terms of extent of reaction, is

$$K_a = \frac{y_{\text{MeOH}}}{y_{\text{CO}}(y_{\text{H}_2})^2} \frac{1}{P^2} = \frac{\dot{\xi}(100 - 2\dot{\xi})^2}{(30 - \dot{\xi})(65 - 2\dot{\xi})^2} \frac{1}{P^2}$$

To find K_a , we first calculate

$$\Delta \hat{G}_r^\circ = -162.32 + 137.27 = -25.05 \text{ kJ/gmol}$$

$$\Delta \hat{H}_r^\circ = -200.94 + 110.53 = -90.41 \text{ kJ/gmol}$$

At 298 K,

$$K_a = \exp\left(\frac{25,050}{8.314 \times 298}\right) = 24605$$

From the van't Hoff equation, at the reaction temperature of 473 K

$$\ln K_a = -\frac{1}{8.314} \left[\frac{-25050 + 90410}{298} - \frac{90410}{473} \right] = -3.39$$

$$K_a = 0.0337$$

The reactor pressure is 4925 kPa, or 40.6 atm. We need to convert to atm, to be consistent with the standard state for the Gibbs energy of reaction

$$K_a P^2 = 0.0337 (40.6)^2 = 55.55 = \frac{\xi(100 - 2\xi)^2}{(30 - \xi)(65 - 2\xi)^2}$$

We know that the extent of reaction must be less than 30 and more than 0. Using an equation solver, we find the root of the equation as:

$$\xi = 25$$

Inserting this value into the material balance equations, we find that the reactor outlet flows are (in kmol/h):

$$\dot{n}_{CO,out} = 5$$

$$\dot{n}_{H_2,out} = 15$$

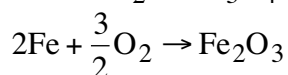
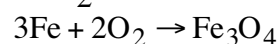
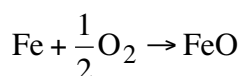
$$\dot{n}_{MeOH,out} = 25$$

$$\dot{n}_{N_2,out} = 5$$

$$\dot{n}_{out} = 50$$

P4.34

Assume the reactions are between Fe and oxygen in the air. The three possible reactions are:



(Note: for these reactions to “go”, water is also required. However, water acts as an intermediate, as a reactant in the formation of $\text{Fe}(\text{OH})_2$, and then as a product in the further oxidation of $\text{Fe}(\text{OH})_2$ to “rust”.)

Since Fe and O_2 are elements in their normal state of aggregation, and we are interested in the reaction equilibrium at room temperature (approximately 298 K), we can say simply that

$\Delta \hat{G}_r = \Delta \hat{G}_f^\circ$. From Table B.3, we see that Fe_3O_4 has the most negative $\Delta \hat{G}_f^\circ$ and should therefore be the dominant form of “rust”.

Both Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) are found naturally in iron ores, but Fe_2O_3 (hematite) is the most common form of rust. This is due to the role of water – hydration of Fe_2O_3 produces a stable complex.

P4.35

The soil is a batch system. To find an expression for m as a function of t , we return to the differential material balance equation:

$$\frac{dm}{dt} = -\dot{R}_{\text{deg}} = -0.012m$$

Collecting terms and using the initial condition that $m = m_{\text{sys},0} = 0.75$ at $t = 0$, we find

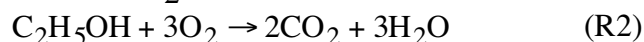
$$\begin{aligned}\frac{dm}{m} &= -0.012dt \\ \int_{m_{\text{sys},0}}^m \frac{dm}{m} &= -\int_0^t 0.012dt \\ m &= m_{\text{sys},0}e^{-0.012t} = 0.75e^{-0.012t}\end{aligned}$$

We are interested in the time at which the mass of atrazine has dropped to one-tenth of its original value, or

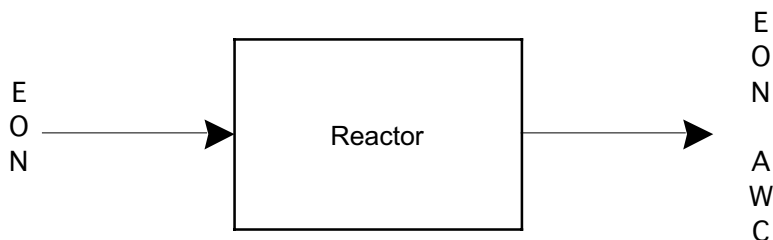
$$\begin{aligned}\frac{m}{m_{\text{sys},0}} &= 0.1 = e^{-0.012t} \\ t &= 192 \text{ days}\end{aligned}$$

P4.36

The two reactions of interest are:



A sketch of the process, with E = ethanol, O = oxygen, N = nitrogen, A = acetaldehyde, W = water, and C = carbon dioxide, is:



There are 9 stream variables plus 2 system (reaction) variables, or 11 variables all together. For information we have 1 specified flow, 2 specified compositions (mole ratio of E to O in feed, and mole ratio of O to N in feed because we assume air is source of oxygen), and 2 system performance specifications. These 5 constraints plus 6 material balance equations fully specify the problem.

The specifications are written (with all flows in kgmol/h) as

$$\begin{aligned}\dot{n}_{A,out} &= 1200 \\ \frac{\dot{n}_{E,in}}{\dot{n}_{O,in}} &= \frac{8}{3} \\ \frac{\dot{n}_{N,in}}{\dot{n}_{O,in}} &= \frac{79}{21} \\ f_{CE} &= 0.25 = \frac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{E,in}} \\ s_{E \rightarrow A} &= 0.6 = \frac{\dot{\xi}_1}{\dot{\xi}_1 + \dot{\xi}_2}\end{aligned}$$

Now we write a material balance equation for acetaldehyde :

$$\dot{n}_{A,out} = 1200 = \dot{\xi}_1$$

From selectivity specification:

$$s_{E \rightarrow A} = 0.6 = \frac{\dot{\xi}_1}{\dot{\xi}_1 + \dot{\xi}_2} = \frac{1200}{1200 + \dot{\xi}_2}, \text{ therefore } \dot{\xi}_2 = 800$$

From conversion specification:

$$f_{CE} = 0.25 = \frac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{E,in}} = \frac{1200 + 800}{\dot{n}_{E,in}}, \text{ therefore } \dot{n}_{E,in} = 8000$$

From composition specification:

$$\begin{aligned}\frac{\dot{n}_{E,in}}{\dot{n}_{O,in}} &= \frac{8}{3}, \text{ therefore } \dot{n}_{O,in} = \frac{3}{8}(8000) = 3000 \\ \frac{\dot{n}_{N,in}}{\dot{n}_{O,in}} &= \frac{79}{21}, \text{ therefore } \dot{n}_{N,in} = \frac{79}{21}(3000) = 11,285\end{aligned}$$

Now, from remaining material balances:

$$\begin{aligned}\dot{n}_{N,out} &= \dot{n}_{N,in} = 11,285 \\ \dot{n}_{E,out} &= 8000 - 1200 - 800 = 6000 \\ \dot{n}_{O,out} &= 3000 - 0.5(1200) - 3(800) = 0 \\ \dot{n}_{C,out} &= 2(800) = 1600 \\ \dot{n}_{W,out} &= 1200 + 3(800) = 3600\end{aligned}$$

Some points of comparison:

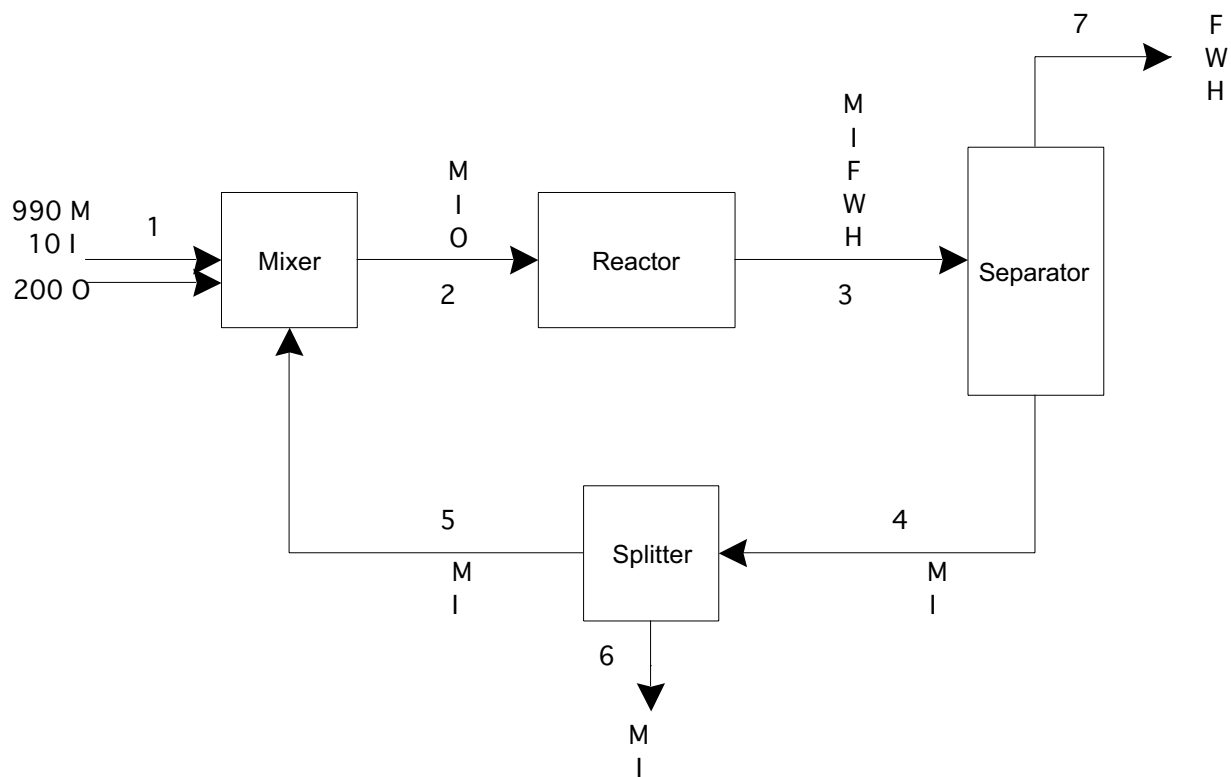
Both catalysts achieve only 25% conversion of ethanol, so both will require the same amount of recycle.

The catalyst in P4.36 operates at greater air flow rates. This will require a larger reactor to handle this increase in volumetric flow rate (assuming the kinetics are similar), thus increasing the capital cost of the reactor. The advantage goes to the Example 4.13 catalyst.

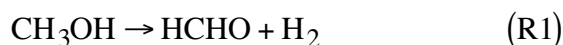
A significant quantity of the byproduct acetic acid is produced with the 4.13 catalyst, while CO_2 is the byproduct unique to catalyst P4.36. If there is a substantial market for acetic acid, then this is an advantage for the 4.13 catalyst. However, separating acetic acid from acetaldehyde and from water is more difficult than is separating CO_2 . Separation costs are likely therefore to be higher for the 4.13 catalyst. A more detailed analysis of the market value of acetic acid, and of the feasibility and cost of recovering acetic acid, is required before a final judgment can be made.

P4.37

The flow diagram, with M for methanol, I for inert, O for oxygen (O_2), F for formaldehyde, H for hydrogen (H_2), W for water, is shown., with streams numbered and labeled, and flows shown as kgmol/h.



The two balanced chemical equations are:



We are given two flow specifications:

$$\dot{n}_{M1} + \dot{n}_{I1} = 100$$

$$\dot{n}_{O1} = 200$$

$$\text{2 stream composition specification: } \frac{\dot{n}_{I5}}{\dot{n}_{M5}} = \frac{10}{100} \quad (\text{max})$$

$$\frac{\dot{n}_{I1}}{\dot{n}_{M1}} = \frac{1}{99}$$

$$\text{two splitter restrictions: } \frac{\dot{n}_{I4}}{\dot{n}_{M4}} = \frac{\dot{n}_{I5}}{\dot{n}_{M5}} = \frac{\dot{n}_{I6}}{\dot{n}_{M6}} = \frac{10}{100}$$

$$\text{a system performance specification: } f_{CM} = 0.25 = \frac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{M2}}$$

We also know from the problem statement that all the oxygen is consumed by reaction, and we know by material balance around the mixer that the oxygen feed to the reactor in stream 2 is 200 kgmol/h. Therefore:

$$f_{CO} = 1.0 = \frac{-\nu_{O2}\dot{\xi}_2}{\dot{n}_{O2}} = \frac{0.5\dot{\xi}_2}{200} \quad \text{or} \quad \dot{\xi}_2 = 400.$$

From this, and material balances on water around the reactor and the separator, we find

$$\dot{n}_{W3} = \dot{n}_{W7} = \nu_{W2}\dot{\xi}_2 = 400$$

With inerts that are purged, it's often useful to group everything together into one system and write the material balance equation around the entire process. From this, we find:

$$\dot{n}_{I1} = \dot{n}_{I6} = 10$$

Now, from the stream composition specification and splitter restriction:

$$\dot{n}_{M6} = 100$$

(a) Since stream 6 is the only stream where methanol leaves the process, we can calculate the overall conversion of methanol to products:

$$f_{CM,overall} = \frac{\dot{n}_{M1} - \dot{n}_{M6}}{\dot{n}_{M1}} = \frac{990 - 100}{990} = 0.90$$

Also

$$f_{CM,overall} = 0.90 = \frac{v_{M1}\dot{\xi}_1 + v_{M2}\dot{\xi}_2}{\dot{n}_{M1}} = \frac{\dot{\xi}_1 + 400}{990}$$

Therefore

$$\dot{\xi}_1 = 490$$

(b) The formaldehyde production rate is

$$\dot{n}_{F3} = \dot{n}_{F7} = v_{F1}\dot{\xi}_1 + v_{F2}\dot{\xi}_2 = 490 + 400 = 890$$

(c) and (d) We return to the single-pass conversion specification to find the methanol feed rate to the reactor:

$$f_{CM} = 0.25 = \frac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{M2}} = \frac{490 + 400}{\dot{n}_{M2}}$$
$$\dot{n}_{M2} = 3560$$

Since the fresh methanol feed rate is 990 kgmol/h, the recycle rate must be (from a material balance around the mixer)

$$3560 = 990 + \dot{n}_{M5}$$
$$\dot{n}_{M5} = 2570$$

And, from a material balance around the reactor

$$\dot{n}_{M3} = (1 - f_{CM})\dot{n}_{M2} = 0.75(3560) = 2670$$

So the purge:recycle ratio is

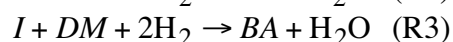
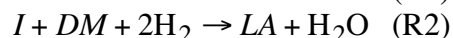
$$\frac{\dot{n}_{M6}}{\dot{n}_{M5}} = \frac{100}{2570} = 0.039$$

and the recycle:fresh methanol feed ratio is

$$\frac{\dot{n}_{M5}}{\dot{n}_{M1}} = \frac{2570}{990} = 2.6$$

P4.38

Let's write the balanced reactions in shorthand as:



where B = butene, I = aldehyde intermediate, DM = dimethylamine, LA = linear amine, and BA = branched amine. Finally, we will let TA = total amines = BA + LA.

Since all the conversion of dimethylamine is 100%, there are 0 millimoles dimethylamine remaining at the end of the experiment. From a material balance,

$$n_{DM,f} - n_{DM,0} = 0 - 15 = -\xi_2 - \xi_3 - \xi_4$$

or

$$\xi_2 + \xi_3 + \xi_4 = 15$$

(We are implicitly assuming that the stoichiometric coefficient of dimethylamine in the unwanted reactions is 1.)

The initial feed of butene was 1.2×15 , or 18 mmol. Based on the first 3 reactions, we see that one mole butene is consumed per mole dimethylamine consumed. So, neglecting the unknown minor byproduct reactions, we estimate that there should be $18 - 15$ or 3 mmol butene remaining.

Since dimethylamine is the limiting reactant, we presume that the selectivity is based on dimethylamine.

At 100°C,

$$s_{DM \rightarrow TA} = \frac{\xi_2 + \xi_3}{\xi_2 + \xi_3 + \xi_4} = 0.54 = \frac{\xi_2 + \xi_3}{15}, \text{ or } \xi_2 + \xi_3 = 8.1 \text{ mmol}$$

$$s_{DM \rightarrow LA} = \frac{\xi_2}{\xi_2 + \xi_3 + \xi_4} = 0.52 = \frac{\xi_2}{15}, \text{ or } \xi_2 = 7.8 \text{ mmol}$$

Therefore, $\xi_3 = 0.3$ mmol, and $\xi_4 = 6.9$ mmol

At 120°C,

$$s_{DM \rightarrow TA} = 0.77 = \frac{\xi_2 + \xi_3}{15}, \text{ or } \xi_2 + \xi_3 = 11.55 \text{ mmol}$$

$$s_{DM \rightarrow LA} = 0.60 = \frac{\xi_2}{15}, \text{ or } \xi_2 = 9 \text{ mmol}$$

Therefore, $\xi_3 = 2.55$ mmol, and $\xi_4 = 3.45$ mmol

At 140°C,

$$s_{DM \rightarrow TA} = 0.98 = \frac{\xi_2 + \xi_3}{15}, \text{ or } \xi_2 + \xi_3 = 14.7 \text{ mmol}$$

$$s_{DM \rightarrow LA} = 0.65 = \frac{\xi_2}{15}, \text{ or } \xi_2 = 9.75 \text{ mmol}$$

Therefore, $\xi_3 = 4.95$ mmol, and $\xi_4 = 0.3$ mmol

We summarize our estimates of the content of the reactor at the end of the run:

T (°C)	mmoles LA	mmoles BA	mmoles TA	LA/BA ratio	mmoles byproducts
100	7.8	0.3	8.1	26	6.9
120	9	2.55	11.55	3.53	3.45
140	9.75	4.95	14.7	1.97	0.3

The lower operating temperature produces a much higher ratio of the desired linear amine to the undesired branched amine, but also produces the greatest quantity of (unknown) byproducts. The final selection of the best operating temperature depends on the answers to a couple of questions:

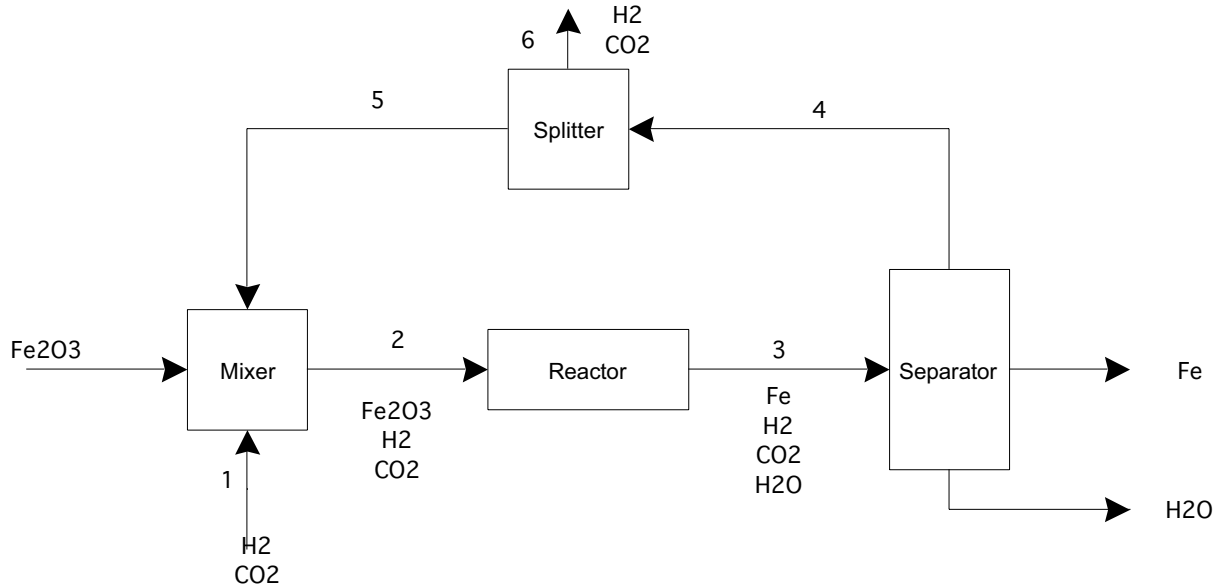
1. How difficult is it to separate branched from linear amines? If this is a difficult separation (which we might suspect), then the lower reaction temperature is attractive.
2. How difficult is it to separate the byproducts from the amines? This is likely to be an easier separation than that of branched from linear amine.
3. Is there a market for the branched amines? If so, then the highest operating temperature is attractive, since we get more total linear amines and a useful byproduct.
4. Are the byproducts toxic or hazardous? If so, then clearly the highest operating temperature is the better choice.
5. Is (R3) reversible? If so, then we might be able to convert branched to linear amines by separating the branched amines and recycling them.

P4.39

Balanced reaction: $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$

Convert basis to molar units: $\frac{1 \text{ ton Fe}_2\text{O}_3}{\text{h}} \times \frac{2000 \text{ lb}}{\text{ton}} \times \frac{1 \text{ lbmol}}{160 \text{ lb}} = \frac{12.5 \text{ lbmol Fe}_2\text{O}_3}{\text{h}}$

Flow diagram:



First look at system overall. Since all the Fe_2O_3 is consumed, $\dot{\xi} = 12.5 \text{ lbmol/h}$, and therefore Fe produced is 25 lbmol/h or 1400 lb/h and H_2O produced is 37.5 lbmol/h or 675 lb/h. Neither Fe or H_2O are in the recycle stream, so the remaining balances are trivial to solve.

Now consider just the H_2 and CO_2 flows. Let $\text{H} = \text{H}_2$ and $\text{C} = \text{CO}_2$. We have some stream specifications:

$$\frac{\dot{n}_{C1}}{\dot{n}_{H1}} = \frac{1}{99}$$

$$\frac{\dot{n}_{H5} + \dot{n}_{C5}}{\dot{n}_{H1} + \dot{n}_{C1}} = 5$$

$$\frac{\dot{n}_{C2}}{\dot{n}_{H2} + \dot{n}_{C2}} = 0.035$$

For CO_2 , from material balances around the mixer, reactor, separator and splitter:

$$\dot{n}_{C1} + \dot{n}_{C5} = \dot{n}_{C2}$$

$$\dot{n}_{C2} = \dot{n}_{C3}$$

$$\dot{n}_{C3} = \dot{n}_{C4}$$

$$\dot{n}_{C5} = f_S \dot{n}_{C4}$$

where f_S is the fractional split.

For H_2 , again working around the loop

$$\begin{aligned}\dot{n}_{H1} + \dot{n}_{H5} &= \dot{n}_{H2} \\ \dot{n}_{H3} &= \dot{n}_{H2} - 3(12.5) = \dot{n}_{H2} - 37.5 \\ \dot{n}_{H4} &= \dot{n}_{H3} \\ \dot{n}_{H5} &= f_S \dot{n}_{H4}\end{aligned}$$

We have 11 equations in 11 unknowns (10 flows + 1 fractional split). There are many ways to solve this; one easy way is to set up an EXCEL spreadsheet. We will insert initial guess values of f_S and \dot{n}_{H1} , solve for the other flows, then let SOLVER find the best values of f_S and \dot{n}_{H1} .

The solution is summarized in the table (all flows in lbmol/h).

	Feed	1	2	3	4	5	6	Product
Fe ₂ O ₃	12.5		12.5					
H ₂		49.5	289.5	252	252	240	12	
CO ₂		0.5	10.5	10.5	10.5	10	0.5	
Fe				25				25
H ₂ O				37.5				37.5

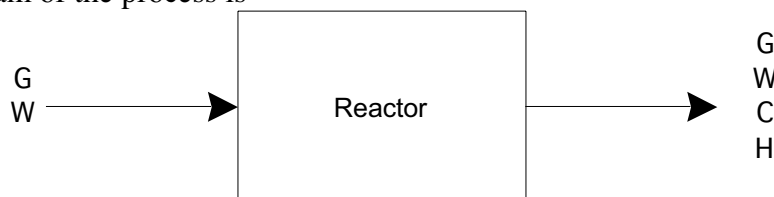
The fractional split f_S is 0.9524, and the overall conversion of hydrogen is 0.7576.

P4.40

The balanced reaction is



A flow diagram of the process is



where G = glycerol, W = water, C = carbon dioxide, and H = hydrogen.

There are 6 stream variables plus 1 system variable. We have 1 specified flow rate, 2 specified compositions, and 4 material balances, so $\text{DOF} = (6 + 1) - (1 + 2 + 4) = 0$.

The units are not consistent: the glycerol flow rate is given in g/h but the ratio of water:glycerol is given in molar units. We have a reaction with known stoichiometric coefficients, so we convert to units of gmol/h.

$$\begin{aligned}\dot{n}_{G,in} &= \frac{150 \text{ g/h}}{92 \text{ g/gmol}} = 1.63 \text{ gmol/h} \\ \dot{n}_{W,in} &= 5\dot{n}_{G,in} = 5 \times 1.63 = 8.15 \text{ gmol/h}\end{aligned}$$

We write 4 material balance equations (all in units of gmol/h):

$$\begin{aligned}\dot{n}_{G,out} &= \dot{n}_{G,in} - \dot{\xi} = 1.63 - \dot{\xi} \\ \dot{n}_{W,out} &= \dot{n}_{W,in} - 3\dot{\xi} = 8.15 - 3\dot{\xi} \\ \dot{n}_{C,out} &= 3\dot{\xi} \\ \dot{n}_{H,out} &= 7\dot{\xi}\end{aligned}$$

From the remaining stream composition specification, we write:

$$\frac{\dot{n}_{H,out}}{\dot{n}_{out}} = 0.54, \text{ where } \dot{n}_{out} = (1.63 + 8.15) - \dot{\xi} - 3\dot{\xi} + 3\dot{\xi} + 7\dot{\xi} = 9.78 + 6\dot{\xi}$$

Therefore, $\frac{\dot{n}_{H,out}}{\dot{n}_{out}} = 0.54 = \frac{7\dot{\xi}}{9.78 + 6\dot{\xi}}$, and $\dot{\xi} = 1.40$ gmol/h.

The fractional conversion of glycerol is: $f_{CG} = \frac{\dot{\xi}}{\dot{n}_{G,in}} = \frac{1.40}{1.63} = 0.86$

The equilibrium constant for this gas-phase reaction is

$$K_a = \frac{(y_C)^3 (y_H)^7}{(y_G)(y_W)^3} P^6 = \frac{(3\dot{\xi})^3 (7\dot{\xi})^7}{(1.63 - \dot{\xi})(8.15 - 3\dot{\xi})^3 (9.78 + 6\dot{\xi})^6} P^6$$

where we calculated the expression on the rhs from the material balances, recognizing that the mole fraction of a compound is simply the molar flow rate of that compound divided by the total molar flow rate. We can answer the question about whether the reactor outlet is at equilibrium in 2 ways:

1. The easy(er) way. Plug in the value $\dot{\xi} = 1.40$ gmol/h, obtained from our process flow calculations, and $P = 1.2$ atm, into the rhs of the equilibrium equation and compare the result to the known K_a . If less, then we are not at equilibrium. When I do this I calculate the rhs of the equilibrium expression to be 3.75, which is less than 55, so we are not at equilibrium.

2. The hard(er) way. Use the equilibrium expression above, with $P = 1.2$ atm, set $K_a = 55$, and solve for the extent of reaction at equilibrium. Compare to that calculated above. When I do this (which is done on a spreadsheet, and carefully, because there are multiple roots!), I find $\dot{\xi} = 1.574$ gmol/h. The equilibrium conversion is greater than the observed conversion, so the system is not at equilibrium.

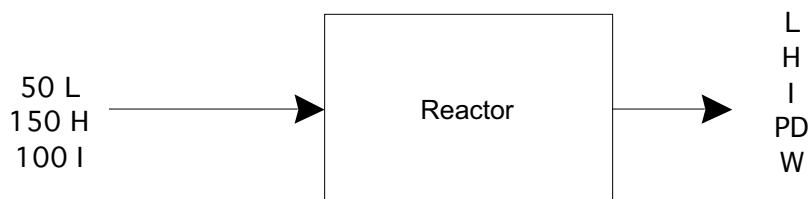
From our solution method (2) we can calculate the fractional conversion of glycerol at equilibrium to be $(1.574/1.63)$ or 0.97, and the mole fraction of hydrogen at equilibrium to be $(7*1.574/(9.78+6*1.574))$, or 0.57.

Reaching equilibrium at these reactor conditions will require increasing the residence time in the reactor. Increasing the reactor temperature might help, as usually the kinetics of reaction increase with temperature, but we don't know the effect of temperature on the equilibrium constant.

To increase the equilibrium conversion of glycerol, we can (1) decrease P or (2) increase the amount of water fed to the reactor. For example, if $P = 1$ atm, $\dot{\xi} = 1.60$ gmol/h. If the water:glycerol ratio increases to 10:1, $\dot{\xi} = 1.63$ gmol/h, and we get essentially 100% conversion. Of course we pay for this in that we need to process a lot more water.

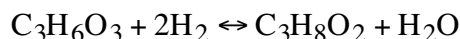
P4.41

The flow diagram is



with L = lactic acid, H = hydrogen, I = inert, PD = propanediol, and W = water, and flows in gmol/h. The reactor outlet is assumed to be at equilibrium and at 5 atm.

The balanced reaction is



For this gas-phase reaction, $K_a P = 3.2 \text{ atm}^{-1} \times 5 \text{ atm} = \frac{y_{PD} y_W}{(y_H)^2 y_L}$

The material balance equations for this reactor operating at steady-state are:

$$\dot{n}_L = 50 - \dot{\xi}$$

$$\dot{n}_H = 150 - 2\dot{\xi}$$

$$\dot{n}_I = 100$$

$$\dot{n}_{PD} = \dot{\xi}$$

$$\dot{n}_W = \dot{\xi}$$

$$\dot{n} = 300 - \dot{\xi}$$

where all the unknown flows are the outlet streams. Using these equations we can rewrite the mole fractions (in the K_a equation) in terms of the extent of reaction:

$$16 = \frac{y_{PD} y_W}{(y_H)^2 y_L} = \frac{\dot{\xi}^2 (300 - \dot{\xi})}{(150 - 2\dot{\xi})^2 (50 - \dot{\xi})}$$

Solving for the physically reasonable root, we find

$$\dot{\xi} = 42.8 \text{ gmol/h}$$

The fractional conversion of lactic acid $f_{CL} = \frac{42.8}{50} = 0.856$

The reactor outlet composition is 2.8 mol% lactic acid, 25 mol% hydrogen, 16.6 mol% propanediol, 16.6 mol% water, and 38.9 mol% inert.

Qualitatively, increasing inert concentration would increase total moles; from our equilibrium expression we see that this would decrease extent of reaction and therefore conversion. Decreasing pressure would decrease conversion. We can see this based on Le Chatelier's principle, or by examining the P dependence in the equilibrium expression. (In a reaction where there is no change in moles with reaction, there would be no dependence on P or on inerts!)

Quantitatively, let's see what happens if the flow rate of I doubles, to 200. The equilibrium expression becomes:

$$16 = \frac{y_{PD}y_W}{(y_H)^2 y_L} = \frac{\dot{\xi}^2(400 - \dot{\xi})}{(150 - 2\dot{\xi})^2(50 - \dot{\xi})}$$

for which we find the solution

$$\dot{\xi} = 41.4 \text{ gmol/h}$$

If P drops to 2 atm, the equilibrium expression becomes:

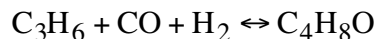
$$6.4 = \frac{y_{PD}y_W}{(y_H)^2 y_L} = \frac{\dot{\xi}^2(300 - \dot{\xi})}{(150 - 2\dot{\xi})^2(50 - \dot{\xi})}$$

and we find

$$\dot{\xi} = 38.6 \text{ gmol/h}$$

P4.42

The reaction is



Let's derive a general expression for the gas-phase reaction, written in terms of molar feed rates and extent of reaction, with P = propylene, C = CO, H = hydrogen, and B = butyraldehyde. We develop a "mole table":

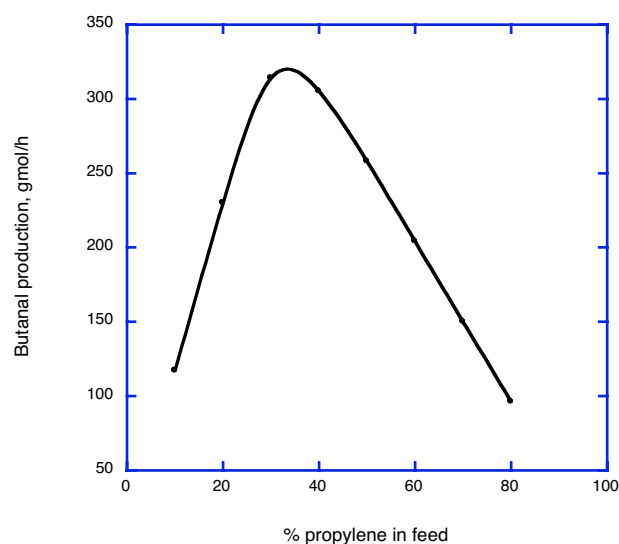
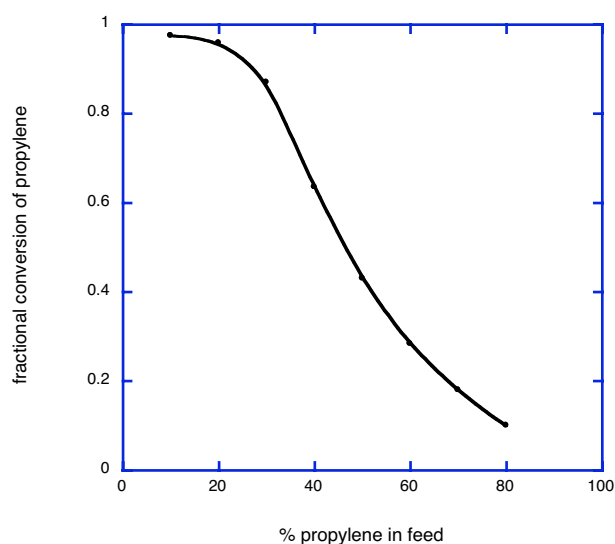
compound	$\dot{n}_{i,out}$	$y_i = \frac{\dot{n}_{i,out}}{\dot{n}_{out}}$
C_3H_6	$\dot{n}_{P,in} - \dot{\xi}$	$\frac{\dot{n}_{P,in} - \dot{\xi}}{\dot{n}_{in} - 2\dot{\xi}}$
CO	$\dot{n}_{C,in} - \dot{\xi}$	$\frac{\dot{n}_{C,in} - \dot{\xi}}{\dot{n}_{in} - 2\dot{\xi}}$
H_2	$\dot{n}_{H,in} - \dot{\xi}$	$\frac{\dot{n}_{H,in} - \dot{\xi}}{\dot{n}_{in} - 2\dot{\xi}}$
C_4H_8O	$\dot{\xi}$	$\frac{\dot{\xi}}{\dot{n}_{in} - 2\dot{\xi}}$
total	$\dot{n}_{in} - 2\dot{\xi}$	1

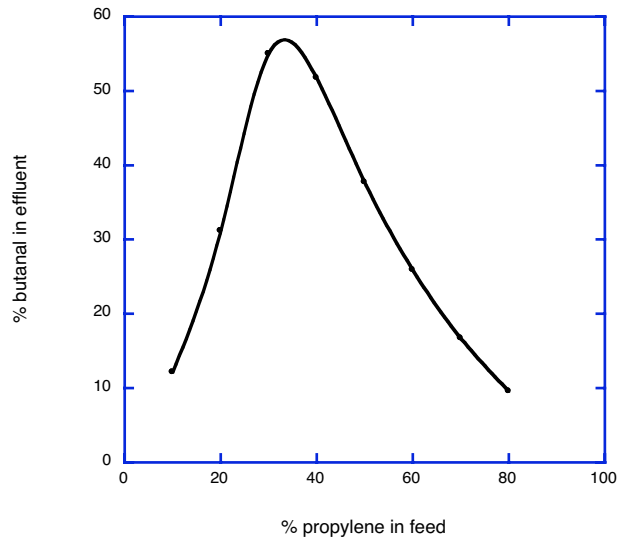
From this we find:

$$K_a = \frac{y_B}{y_P y_C y_H} \frac{1}{P^2} = \frac{\dot{\xi}(\dot{n}_{in} - 2\dot{\xi})^2}{(\dot{n}_{P,in} - \dot{\xi})(\dot{n}_{C,in} - \dot{\xi})(\dot{n}_{H,in} - \dot{\xi})} \frac{1}{P^2} = 8 \text{ atm}^{-2}$$

To proceed, we set $P = 5 \text{ atm}$ and $\dot{n}_{in} = 1200 \text{ gmol/h}$. For our first analysis, we are given an inlet composition of 20% P, 40% C and 40% H, so we set $\dot{n}_{P,in} = 240 \text{ gmol/h}$, $\dot{n}_{C,in} = 480 \text{ gmol/h}$, and $\dot{n}_{H,in} = 480 \text{ gmol/h}$. At these conditions, we calculate a fractional conversion of propylene of 0.958, butanal production rate of 230 gmol/h, and 31.1 mol% butanal in reactor effluent.

We continue with similar calculations at different mol% propylene. Results are summarized in graphical form. (You need to be careful when finding the roots of the equation. There are several mathematically correct roots that are not physically reasonable.)





The maximum butanal production rate is obtained when the propylene:CO:H₂ ratio is stoichiometric (1:1:1, or 33.3 mol% propylene in feed). The highest butanal purity in the reactor effluent also occurs at the stoichiometric feed conditions. This is advantageous because separations costs are generally lower if the effluent is more concentrated in the desired product. The greatest fractional conversion is obtained at the lowest propylene mol%, when CO and H₂ are fed in excess. If propylene is very expensive and/or difficult to recover and recycle, then one might want to operate at the lowest feasible propylene in the feed.

P4.43

From data in Appendix B, we calculate:

$$\Delta \hat{H}_r^\circ = (-1)(-110.5) + (-1)(-241.8) + (-393.5) = -41.2 \text{ kJ/gmol}$$

$$\Delta \hat{G}_r^\circ = (-1)(-137.3) + (-1)(-228.6) + (-394.4) = -28.5 \text{ kJ/gmol}$$

From the van't Hoff equation

$$\ln K_a = -\frac{1}{8.314} \left[\frac{-28500 + 41200}{298} - \frac{41200}{T} \right] = -5.126 + \frac{4955}{T}$$

K_a as a function of T was calculated in a spreadsheet

T(°C)	T(K)	K _a
100	373	3491.83
200	473	210.54
300	573	33.83
400	673	9.36
500	773	3.61
600	873	1.73
700	973	0.97
800	1073	0.60
900	1173	0.41
1000	1273	0.29

We know that

$$K_a = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = \frac{\xi^2}{(1-\xi)^2} \text{ assuming equimolar (1:1) feed of CO and H}_2\text{O.}$$

This equation can be re-written using the quadratic formula and simplifying:

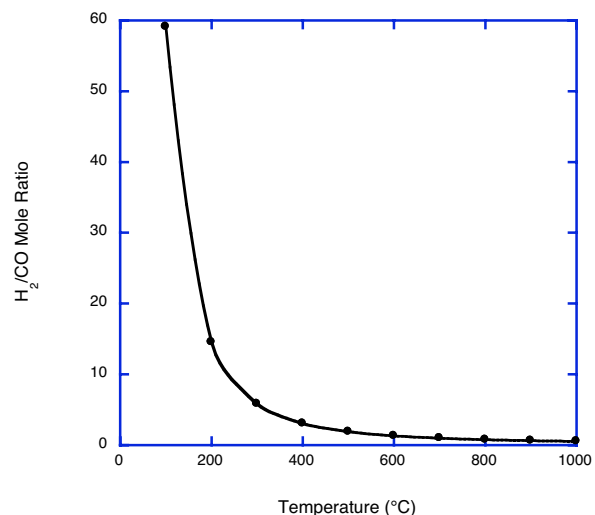
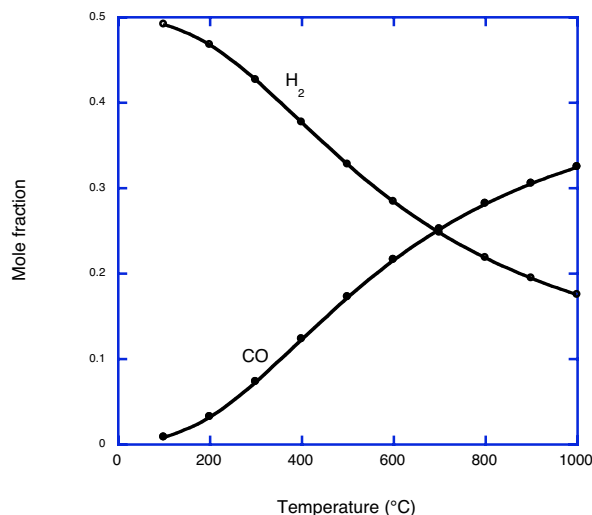
$$\xi = \frac{K_a - \sqrt{K_a}}{K_a - 1} \text{ (from the quadratic formula).}$$

With mole fractions

$$y_{CO} = \frac{1-\xi}{2}$$

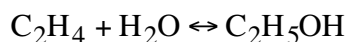
$$y_{H_2} = \frac{\xi}{2}$$

The results are plotted. A reactor temperature of 488 °C gives a 2:1 mole ratio of H₂:CO.



P4.44

The gas-phase reaction is



with an equilibrium expression given as:

$$K_a = \frac{y_{\text{EtOH}}}{y_{\text{E}} y_{\text{W}}} \frac{1}{P}$$

If we choose as a basis 1 gmol/min ethylene fed to the reactor, and specify an equimolar ethylene:water feed ratio, then

$$\dot{n}_{\text{E},out} = 1 - \dot{\xi}$$

$$\dot{n}_{\text{W},out} = 1 - \dot{\xi}$$

$$\dot{n}_{\text{EtOH},out} = \dot{\xi}$$

$$\dot{n}_{out} = 2 - \dot{\xi}$$

and, since $y_i = \dot{n}_{i,out} / \dot{n}_{out}$, we can write the equilibrium equation in terms of the extent of reaction:

$$K_a = \frac{\dot{\xi}(2 - \dot{\xi})}{(1 - \dot{\xi})(1 - \dot{\xi})} \frac{1}{P}$$

Expanding and rearranging, we find that this is a quadratic equation:

$$(K_a P + 1)\dot{\xi}^2 - 2(K_a P + 1)\dot{\xi} + K_a P = 0$$

with a solution from the quadratic formula of:

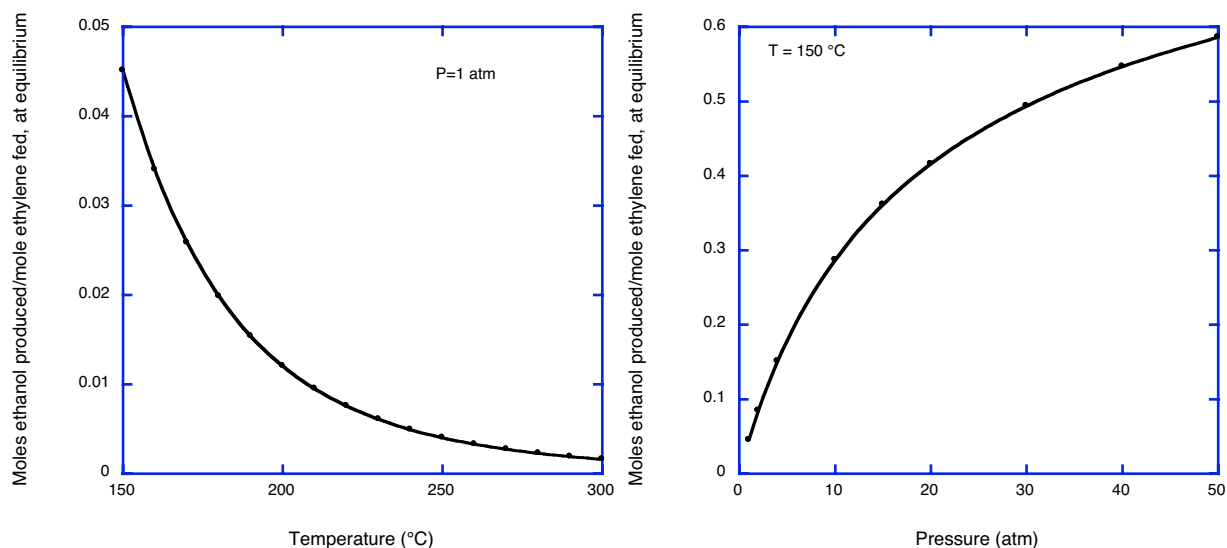
$$\dot{\xi} = \frac{\sqrt{K_a P + 1} \pm 1}{\sqrt{K_a P + 1}}$$

From the data in Table B.3 we calculate the Gibbs energy and enthalpy of reaction:

	$\Delta\hat{G}_f^\circ$ or $\Delta\hat{G}_r^\circ$, kJ/gmol	$\Delta\hat{H}_f^\circ$ or $\Delta\hat{H}_r^\circ$, kJ/gmol
C_2H_4	68.44	52.51
H_2O	-228.59	-241.83
$\text{C}_2\text{H}_5\text{OH}$	-167.85	-234.95
reaction	-7.70	-45.63

$$\ln K_a = -\frac{1}{8.3144} \left[\frac{-7700 + 45,630}{298} - \frac{45630}{T} \right] = -15.31 + \frac{5488}{T}$$

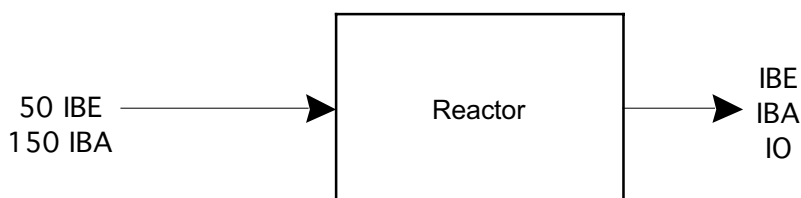
Now if we specify T , we can calculate K_a , and if we also specify P , we can calculate the extent of reaction, which is also the molar flow rate of ethanol produced. These calculations are most easily carried out in a spreadsheet. (You need to pick the correct root of the solution.) The results are graphed below.



Ethanol production rate decreases markedly with increasing temperature, so the reactor should be designed to operate at as low a temperature as feasible. This may be limited by kinetic considerations. Production increases with pressure. So the reaction should be run at a relatively high pressure, constrained by the cost of purchasing higher pressure equipment and the energy cost of compressing gases.

P4.45

On this flow diagram, IBE = isobutene, IBA = isobutane, and IO = iso-octane, and flows are given in gmol/min. The reactor is assumed to operate at steady-state and the outlet flow is assumed to be at equilibrium.



The material balances are

$$\begin{aligned}\dot{n}_{IBE} &= 50 - \dot{\xi} \\ \dot{n}_{IBA} &= 150 - \dot{\xi} \\ \dot{n}_{IO} &= \dot{\xi} \\ \dot{n} &= 200 - \dot{\xi}\end{aligned}$$

where the variables are the unknown outlet flow rates in gmol/min. From these equations we calculate the mole fractions of each component in the outlet stream in terms of the extent of reaction and find

$$K_a = 1.8 \text{ atm}^{-1} = \frac{y_{IO}}{y_{IBE}y_{IBA}} \frac{1}{P} = \frac{\dot{\xi}(200 - \dot{\xi})}{(50 - \dot{\xi})(150 - \dot{\xi})} \frac{1}{4 \text{ atm}}$$

Solving,
 $\dot{\xi} = 41.6 \text{ gmol/min}$

The limiting reactant is isobutene, with

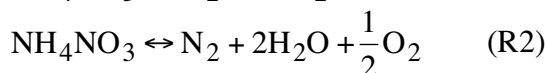
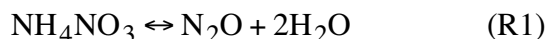
$$f_{C,IBE} = \frac{41.6}{50} = 0.83$$

From the material balances we calculate that the outlet flow rate is 158.4 gmol/min and its composition is 26.3 mol% isobutane, 5.3 mol% isobutene, and 68.4 mol% iso-octane.

(a) To get higher fractional conversion of isobutene I would *decrease* the isobutene/isobutane ratio in the feed and increase P. (b) To get higher mole fraction of iso-octane in the product stream I would *increase* the isobutene:isobutane ratio in the feed to the stoichiometric ratio, and increase P.

P4.46

The balanced reactions are



Only 2 of the 3 reactions are independent. We can see that by, for example, adding (R1) + (R3) to get (R2), or we can use the matrix methods of Chapter 3.

Let's consider (R1) and (R3). (Since only 2 of the reactions are independent, we can pick any 2 for this analysis and should end up with the same answer.) Assume we have 1 gmol ammonium nitrate initially (and no other compounds), and we allow the system to react to reach equilibrium.

$$n_{AN,eq} = 1 - \xi_1$$

$$\begin{aligned}
n_{N_2O,eq} &= \xi_1 - \xi_3 \\
n_{H_2O,eq} &= 2\xi_1 \\
n_{N_2,eq} &= \xi_3 \\
n_{O_2,eq} &= \frac{1}{2}\xi_3
\end{aligned}$$

Let's collect some Gibbs energy and enthalpy of formation data from Table B.3

	$\Delta\hat{G}_f^\circ$ or $\Delta\hat{G}_r^\circ$, kJ/gmol	$\Delta\hat{H}_f^\circ$ or $\Delta\hat{H}_r^\circ$, kJ/gmol
NH ₄ NO ₃ (solid)	-184	-365.56
N ₂ O (vapor)	104.16	82.05
H ₂ O (vapor)	-228.59	-241.83
N ₂	0	0
O ₂	0	0
Reaction 1	-169	-36.05
Reaction 2	-104.16	-82.05

$$\ln K_{a,R1} = -\frac{1}{8.3144} \left[\frac{-169,000 + 36,050}{298} - \frac{36,050}{T} \right] = 53.66 + \frac{4336}{T} \quad (\text{with solid ammonium nitrate})$$

$$\ln K_{a,R2} = -\frac{1}{8.3144} \left[\frac{-104,160 + 82,050}{298} - \frac{82,050}{T} \right] = 8.92 + \frac{9868}{T}$$

Both reactions are highly favorable, and will go essentially to complete conversion at equilibrium ($\xi_1 = \xi_3 = 1$). The equilibrium mixture is 57% water, 29% N₂, and 14% O₂ (2:1:0.5 mole ratio, from stoichiometry).

Ammonium nitrate by itself is quite stable – although the equilibrium is highly favorable, the reaction will not occur in the absence of a triggering agent. In the Texas City tragedy, a ship containing ammonium nitrate exploded (killing over 500 people). It was discovered that carbon from the cellulose in the paper bags used to package the ammonium nitrate triggered the explosion.

Mixing fuel oil with ammonium nitrate on site triggers the explosive detonation of ammonium nitrate. The sudden change from solid to vapor leads to a rapid increase in pressure. Only a small amount of fuel oil is needed to trigger the explosion, so for controlled explosions one would not add a lot of fuel oil. A greater quantity of fuel oil would burn after the initial explosion, causing an enormous amount of destruction.

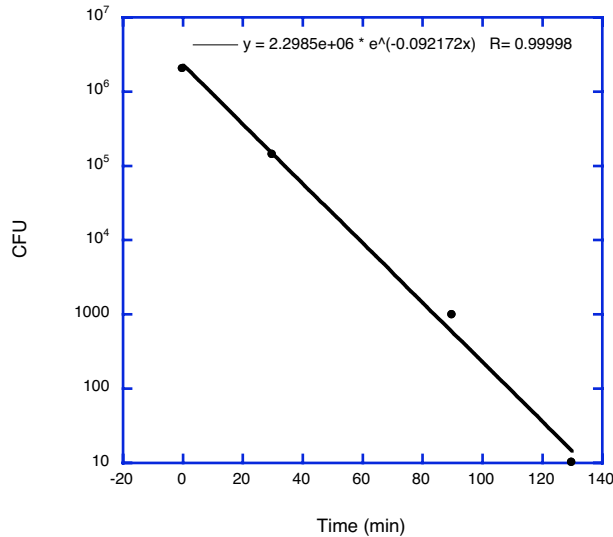
P4.47

The data allow us to calculate the rate of degradation as

$$r_{deg} = \frac{d[cfu]}{dt} = -k_f[cfu], \text{ or, integrating with initial condition that } [cfu]=[cfu]_0 \text{ at } t = 0,$$

$$[cfu] = [cfu]_0 \exp(-k_f t)$$

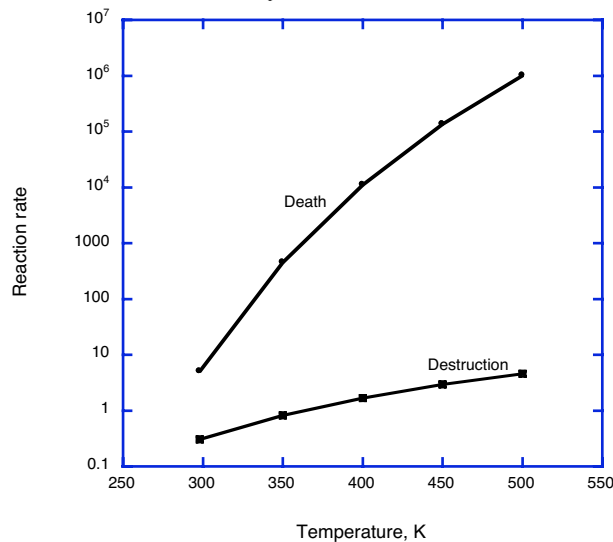
We can fit this equation to the data using nonlinear regression (see for example Appendix A). The estimated rate constant is $k_f = 0.092 \text{ min}^{-1}$.



(One could also take the logarithm of the data and find the slope of $\ln[cfu]$ vs t .)

P4.48

First we calculate \dot{r}_{death} and $\dot{r}_{destruction}$ as a function of T . We will calculate at the initial conditions, where $N_{spore} = 22,000$, and $m_{nutrien} = 50 \text{ mg}$. The results are plotted.



What we observe is that the rate of death increases faster with temperature than does the rate of destruction. To minimize destruction of the nutrient while we maximize death of the spores, we may want to operate at high temperatures and short times.

Now let's apply material balance equations to the sterilizer. The system is batch, and we are interested in the rate of change of spores and of nutrient in the reactor. Let's start with the material balance equation for spores at any instance of time:

$$\frac{dN_{spores}}{dt} = -\dot{r}_{death} = -3 \times 10^9 \exp\left(\frac{-9000}{T}\right) N_{spores} = -k_s N_{spores}$$

where we've used k_s as a short hand for $3 \times 10^9 \exp(-9000/T)$. (The "minus" sign is needed because death leads to a decrease in the number of spores.)

The rate of change in the number of spores is proportional to the number of live spores. We rearrange and then integrate from $t = 0$ to any time t :

$$\begin{aligned} \int_{N_0}^N \frac{dN_{spores}}{N_{spores}} &= - \int_0^t k_s dt \\ \ln\left(\frac{N}{N_0}\right) &= -k_s t \\ \frac{N}{N_0} &= e^{-k_s t} \end{aligned}$$

where N_0 is the initial number of spores and N is the number of spores at time t .

A similar development leads us to

$$\frac{m}{m_0} = e^{-k_n t}$$

where k_n is the rate constant ($5 \exp(-2000/T)$) for the nutrients, m_0 is the initial mass of nutrients in the broth, and m is the mass at any time t .

(a) For 99.999% spore death, $\frac{N}{N_0} = 0.00001 = e^{-k_s t} = e^{-\left[3 \times 10^9 \exp(-9000/T)\right]t}$.

For 50% nutrient loss, $\frac{m}{m_0} = 0.5 = e^{-k_n t} = e^{-\left[5 \exp(-2000/T)\right]t}$. We need to find T and t where both of these equations are satisfied simultaneously. The solution is $T = 402$ K (129°C) and $t = 20$ min.

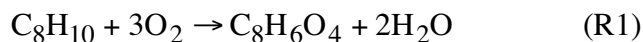
(b) For 99.999% spore death but only 5% nutrient loss, we set $\frac{m}{m_0} = 0.95$ and find that the solution is $T = 473$ K (200°C) and $t = 0.7$ min. To retain nutrients, we operate at high temperature for short times.

For the last part, we shall leave $T = 473 \text{ K}$ (200°C) and $t = 0.7 \text{ min}$, and change the spore death equation to $\frac{N}{N_0} = e^{-k_s t} = e^{-\left[10^{40} \exp(-45000/T)\right]t}$. The nutrient loss remains at 5%, but

$$\frac{N}{N_0} = 0.966 \quad \text{- we've destroyed virtually none of the spores! This is a } \textit{big} \text{ worry.}$$

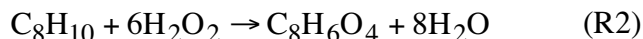
P4.49

The reaction for the conventional process is



$$\text{Atom economy is } \frac{166}{106 + 3(32)} = 0.822$$

The overall reaction for the proposed process is



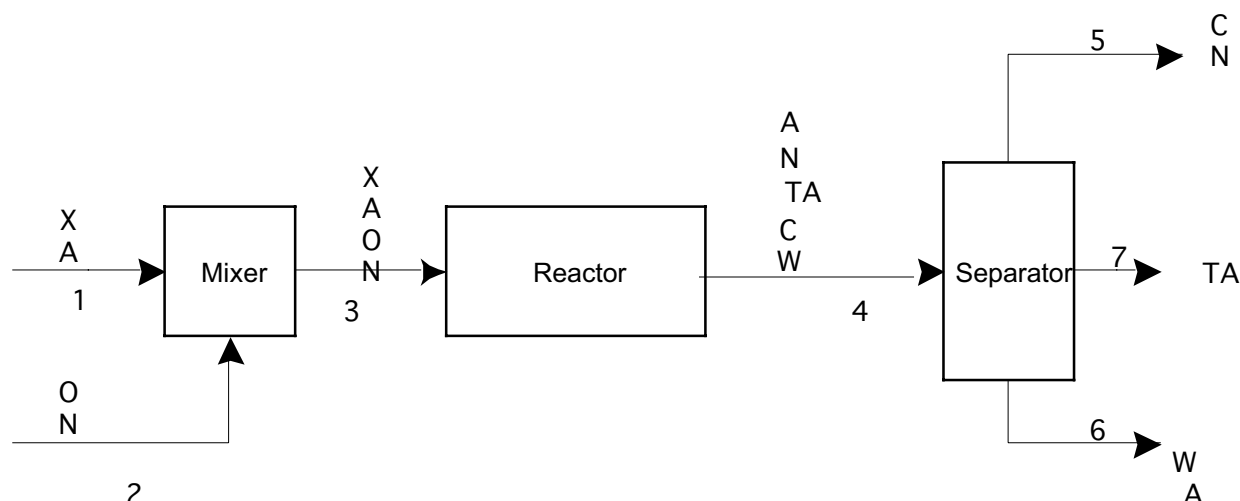
$$\text{Atom economy is } \frac{166}{106 + 6(34)} = 0.535 \text{ (not as good as conventional process).}$$

Conventional process analysis:

In addition to (R1), oxidation of acetic acid occurs:



The flow diagram (with X = xylene, O = oxygen, N = nitrogen, A = acetic acid, C = CO_2 , W = H_2O , TA = terephthalic acid) is



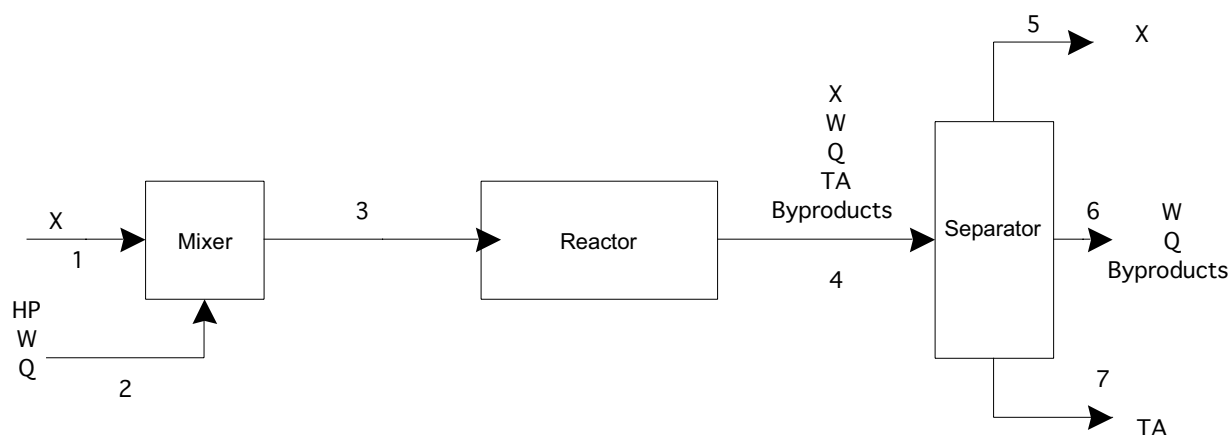
We'll assume (1) stream 1 is 10wt% acetic acid, (2) stream 2 is 21 mol% O₂, 79 mol% N₂ (3) complete conversion of xylene to TA, (4) 10% conversion of acetic acid to CO₂, (5) complete consumption of oxygen by reaction, and (6) perfect separators. The basis is 100 kg/day TA production, or 600 gmol/day TA. From the molar masses of the compounds, we convert stream 1 composition to 600 gmol/day xylene plus 15,000 gmol/day acetic acid. From these assumptions and the material balance equations at steady state, we calculate flows (all in gmol/day):

	1	2	3	4	5	6	7
X	600		600	0			
A	15000		13500	13500		13500	
O		4800	4800	0			
N		18048	18048		18048		
TA				600			600
C				3000	3000		
W				4200		4200	

(Notes: stoichiometric oxygen flow for R1 would be 3 x 600 or 1800 gmol/day. 10% conversion of acetic acid by R3 requires 2 x 0.1 x 15000 = 3000 gmol/day oxygen. The water produced comes from both (R1) and (R3).)

This process has excellent atom economy and yield. Its main drawback is that a significant amount of acetic acid is consumed. If the acetic acid is recycled (which would be necessary), the water would first need to be separated out. How difficult this separation is, remains to be seen.

Connie's process might look like this:



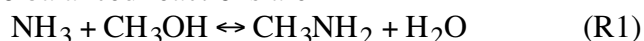
(Notes: Q is the inexpensive catalyst, HP is hydrogen peroxide. With a 70% yield and 90% selectivity, we can calculate that the fractional conversion of xylene is 0.778. For the same production rate of TA, we need to feed $600/0.7$ or 857 gmol/day xylene. About 77.8%, or 667 gmol/day will react, of which 90% will react to the desired product PA. The desired reaction requires 6×600 or 3600 gmol/day HP; likely, the reaction will be run with some excess HP – I assumed 20% above this, and all consumed through either the desired or the side reactions. Water production will be 8×600 or 4800 gmol/day with the desired reaction, plus I estimated the extra HP all reacts to water, which adds 720 gmol/day water produced. We are not given information on how much supercritical water is added. The xylene would be recycled.)

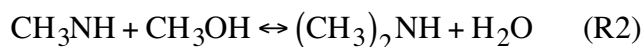
	1	2	3	4	5	6	7
X	857		857	191	191		
HP		4320	4320	0		1350	
W		W	W	W+5520		W+5520	
TA				600			600
byproducts				?		?	

The feasibility of Connie's process depends on (a) the nature of the byproducts – e.g., are they highly toxic, corrosive, or innocuous, (b) the difficulty of separating the unknown byproducts from X and TA, (c) the cost of the catalyst and the feasibility of recycling it or disposing of it, (d) the possibility for either improving the yield or recycling the xylene by tweaking reactor conditions, (e) the expense of hydrogen peroxide compared to air, and (f) the energy cost associated with making water supercritical. The key advantage of Connie's process is that enormous quantities of acetic acid are no longer required, however, there are many questions to be answered before one would get too enthusiastic about the alternative process compared to the tried-and-true.

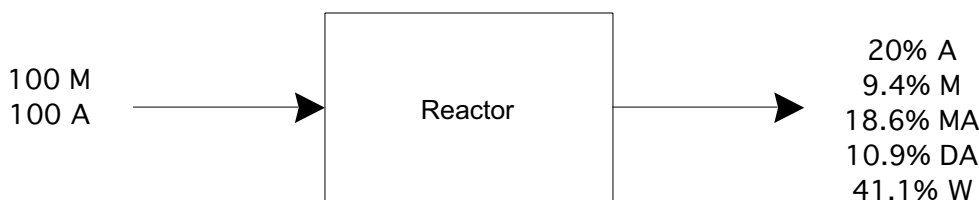
P4.50

The two balanced reactions are





The laboratory reactor flow diagram is shown.



where M = methanol, A = ammonia, MA = methylamine, DA = dimethylamine, and W = water.
From the total mole balance equation at steady state:

$$\begin{aligned} \dot{n}_{out} &= \sum_i \dot{n}_{i,in} + \sum_k \sum_i \nu_{ik} \dot{\xi}_k = \dot{n}_{M,in} + \dot{n}_{A,in} + \dot{\xi}_1 \sum_i \nu_{i1} + \dot{\xi}_2 \sum_i \nu_{i2} \\ &= 100 + 100 + (-1 - 1 + 1 + 1)\dot{\xi}_1 + (-1 - 1 + 1 + 1)\dot{\xi}_2 = 200 \end{aligned}$$

Now we can proceed to check whether the data satisfy the element balance equations.

N: $100 = (0.20 + 0.186 + 0.109)200?$
 $100 = 99?$ (close enough!)

C: $100 = (0.094 + 0.186 + 2 \times 0.109)200?$
 $100 = 99.6?$ (looks good!)

H: $3 \times 100 + 4 \times 100 = (3 \times 0.2 + 4 \times 0.094 + 5 \times 0.186 + 7 \times 0.109 + 2 \times 0.411)200?$
 $700 = 698?$ (yes!)

O: $100 = (0.094 + 0.411)200?$
 $100 = 101?$ (we're done!)

The data all look excellent.

(a) fractional conversion of methanol $f_{CM} = \frac{\dot{n}_{M,in} - \dot{n}_{M,out}}{\dot{n}_{M,in}} = \frac{100 - 0.094 \times 200}{100} = 0.81$

(b) yield of methylamine based on methanol $y_{M \rightarrow MA} = \frac{0.186 \times 200}{100} = 0.37$

(c) selectivity of methylamine based on methanol $s_{M \rightarrow MA} = \frac{0.186 \times 200}{100 - (0.094 \times 200)} = 0.46$

(d) Ammonia participates in (R1) only so it is easiest to calculate the reaction rate r_1 using an ammonia material balance

$$\begin{aligned}\dot{n}_{A,out} &= \dot{n}_{A,in} + \dot{r}_{A1} \\ 0.20 \times 200 &= 100 + \dot{r}_{A1} \\ \dot{r}_{A1} &= -60 \text{ gmol/h}\end{aligned}$$

Since the stoichiometric coefficient = 1 for all compounds, we have

$$-\dot{r}_{A1} = -\dot{r}_{M1} = \dot{r}_{MA1} = \dot{r}_{W1} = \dot{\xi}_1 = 60.$$

(e) Since dimethylamine participates in (R2) only:

$$\dot{n}_{DA,out} = 0.109 \times 200 = \dot{r}_{DA2} = 21.8 \text{ gmol/h}$$

Since the stoichiometric coefficient = 1 for all compounds, then

$$\dot{r}_{DA2} = \dot{r}_{W2} = -\dot{r}_{MA2} = -\dot{r}_{M2} = \dot{\xi}_2 = 21.8.$$

To check if the laboratory reactor is at equilibrium we calculate:

$$\begin{aligned}K_{a1} &= \frac{y_{MA}y_W}{y_M y_A} \\ 4 &= \frac{(0.186)(0.411)}{(0.20)(0.094)}? \\ 4 &= 4.066 \text{ (close enough)}\end{aligned}$$

$$\begin{aligned}K_{a2} &= \frac{y_{DA}y_W}{y_M y_{MA}} \\ 2.5 &= \frac{(0.109)(0.411)}{(0.186)(0.094)}? \\ 2.5 &= 2.56 \text{ (close enough)}\end{aligned}$$

Both calculations show that the reactor effluent is at equilibrium.

In the general case, the material balance equations tell us:

$$\dot{n}_{M,out} = \dot{n}_{M,in} - \dot{\xi}_1 - \dot{\xi}_2$$

$$\dot{n}_{A,out} = \dot{n}_{A,in} - \dot{\xi}_1$$

$$\dot{n}_{MA,out} = \dot{\xi}_1 - \dot{\xi}_2$$

$$\dot{n}_{DA,out} = \dot{\xi}_2$$

$$\dot{n}_{W,out} = \dot{\xi}_1 + \dot{\xi}_2$$

The equilibrium conversion can be calculated from

$$K_{a1} = 4 = \frac{y_{MA}y_W}{y_My_A} = \frac{(\dot{\xi}_1 - \dot{\xi}_2)(\dot{\xi}_1 + \dot{\xi}_2)}{(\dot{n}_{M,in} - \dot{\xi}_1 - \dot{\xi}_2)(\dot{n}_{A,in} - \dot{\xi}_1)} \quad \text{and}$$

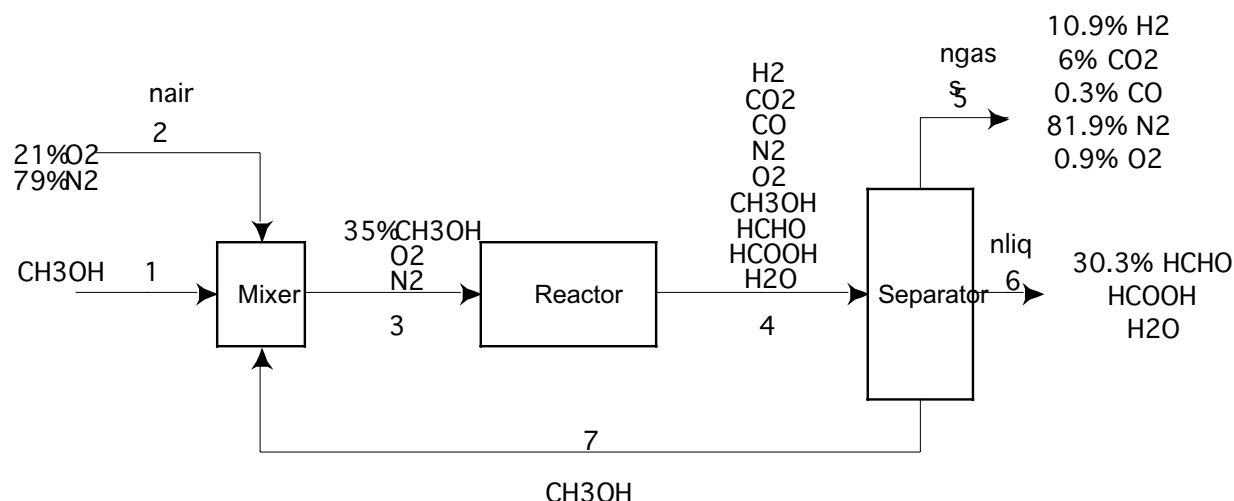
$$K_{a2} = 2.5 = \frac{y_{DA}y_W}{y_{MA}y_M} = \frac{\dot{\xi}_2(\dot{\xi}_1 + \dot{\xi}_2)}{(\dot{\xi}_1 - \dot{\xi}_2)(\dot{n}_{M,in} - \dot{\xi}_1 - \dot{\xi}_2)}$$

where the extents of reaction are those at equilibrium. Now we can use these equations to explore how changing the ammonia:methanol ratio affects yields and reactor outlet concentrations. We do this by fixing $\dot{n}_{A,in}$ and $\dot{n}_{M,in}$ at some desired flows, then solving the two equations simultaneously to find $\dot{\xi}_1$ and $\dot{\xi}_2$ (taking careful note that we find solutions that are physically reasonable), then calculate the desired quantities. Representative calculations are summarized in the table. All rates are in gmol/h.

$\dot{n}_{A,in}$	$\dot{n}_{M,in}$	$\dot{n}_{A,in}/\dot{n}_{M,in}$	$\dot{\xi}_1$	$\dot{\xi}_2$	% MA	MA/DA	$y_{A \rightarrow MA}$	$y_{M \rightarrow MA}$
100	50	2	36.8	8.1	19.0	3.5	0.29	0.57
100	100	1	59.4	21.8	18.8	1.7	0.376	0.376
100	200	0.5	83.2	47.4	11.9	0.75	0.36	0.18
100	400	0.25	95.9	74.0	4.4	0.29	0.22	0.055

Selectivity towards methylamine production, and yield of MA based on MeOH are best at excess ammonia. If methanol is expensive, separations are difficult, and there is no market for dimethylamine, we would likely choose to operate at excess ammonia with recycle. The yield of MA based on ammonia is best at a stoichiometric feed ratio. We might choose to operate at stoichiometric feed ratio if ammonia is expensive or we cannot recycle methanol. Operating at excess methanol does not make sense.

P4.51



There are 8 compounds involved in chemical reactions, and 3 elements (C, H, O). There are at most $8 - 3 = 5$ independent chemical reactions.

Per the flow diagram, using as a basis 100 gmol methanol fed:

No of stream variables	24	No of specified flows	1
No of reaction variables	5	No. of specified compositions	$1+1+4+1=7$
		No. of material balances	$9+9+3=21$
Total variables	29	Total constraints	29

So $\text{DOF} = 29 - 29 = 0$.

We use the methods of Chapter 3 to identify a set of independent chemical equations.

The matrix is (with compounds listed in order of CH_3OH , O_2 , HCHO , HCOOH , CO , CO_2 , H_2O , H_2):

$$\begin{bmatrix} 1 & 0 & 1 & 1 & 1 & 1 & 0 & 0 \\ 4 & 0 & 2 & 2 & 0 & 0 & 2 & 2 \\ 1 & 2 & 1 & 2 & 1 & 2 & 1 & 0 \end{bmatrix}$$

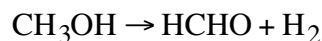
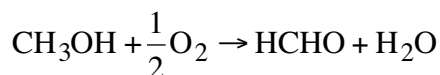
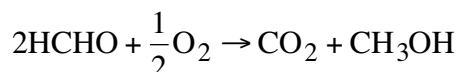
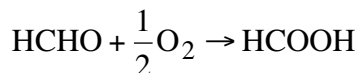
Row reduction gives

$$\begin{bmatrix} 1 & 0 & 0 & 0 & -1 & -1 & 1 & 1 \\ 0 & 1 & 0 & 0.5 & 0 & 0.5 & 0.5 & 0 \\ 0 & 0 & 1 & 1 & 2 & 2 & -1 & -1 \end{bmatrix}$$

Deletion of the 3x3 identity matrix, inversion of the remainder, and addition of a 5 x 5 identity matrix, gives

$$\begin{bmatrix} 0 & 1 & 1 & -1 & -1 \\ -0.5 & 0 & -0.5 & -0.5 & 0 \\ -1 & -2 & -2 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Reading down, we find 5 reactions:



With 9 compounds and 5 reactions but only 4 elements, it is easier to choose elements as compounds. We start with a balance on the inert, N_2 :

$$.79\dot{n}_{air} = 0.819\dot{n}_{gas}$$

Then we write balances on C, H, and O. Since data are given in the form of mole fraction, it is easier to work with mole fractions and total flows as variables.

$$100 = (0.003 + 0.06)\dot{n}_{gas} + (0.303 + x_{FA})\dot{n}_{liq}$$

$$400 = (0.109 \times 2)\dot{n}_{gas} + (0.303 \times 2 + 2x_{FA} + 2x_W)\dot{n}_{liq}$$

$$100 + (0.21 \times 2)\dot{n}_{air} = (0.009 \times 2 + 0.003 + 0.06 \times 2)\dot{n}_{gas} + (0.303 + 2x_{FA} + x_W)\dot{n}_{liq}$$

We have 4 equations in 5 unknowns, but we also know that

$$x_{FA} + x_W + 0.303 = 1$$

We solve to find

$$\begin{aligned}\dot{n}_{air} &= 333 \\ \dot{n}_{gas} &= 322 \\ \dot{n}_{liq} &= 165 \\ x_{FA} &= 0.18 \\ x_W &= 0.516\end{aligned}$$

Production of formaldehyde is 0.303×165 or 50 moles/100 moles methanol fed.
Production of formic acid is 0.18×165 or 30 moles/100 moles methanol fed.

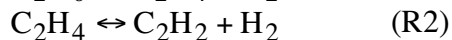
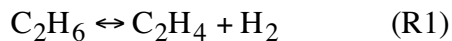
Once we know the air flow rate, we can calculate the flow rate to the reactor, because stream 3 is 35 mol% methanol:

$$\begin{aligned}0.35 &= \frac{\dot{n}_{MeOH,3}}{\dot{n}_{MeOH,3} + 333} \\ \dot{n}_{MeOH,3} &= 179 \\ \dot{n}_3 &= 179 + 333 = 512\end{aligned}$$

Reducing the air:methanol feed rate, reducing conversion in the reactor and increasing the recycle, should lead to less complete oxidation of methanol to formic acid, and therefore greater production of formaldehyde.

P4.52

The two reactions are



From Table B.3, we find

	$\Delta\hat{G}_f^\circ$, kJ/gmol	$\Delta\hat{H}_f^\circ$, kJ/gmol
C_2H_6	-31.92	-83.82
C_2H_4	68.44	52.51
C_2H_2	210.68	228.2
H_2	0	0
Reaction R1	+100.36	+136.33
Reaction R2	+142.24	+175.69

$$\begin{aligned}\ln K_{a1} &= -\frac{1}{8.3144} \left[\frac{100,360 - 136,330}{298} + \frac{136,300}{T} \right] = 14.52 - \frac{16,393}{T} \\ \ln K_{a2} &= -\frac{1}{8.3144} \left[\frac{142,240 - 175,690}{298} + \frac{175,690}{T} \right] = 13.5 - \frac{21,130}{T}\end{aligned}$$

From material balances we calculate:

$$\dot{n}_{EA,out} = \dot{n}_{EA,in} - \dot{\xi}_1$$

$$\dot{n}_{EE,out} = \dot{\xi}_1 - \dot{\xi}_2$$

$$\dot{n}_{A,out} = \dot{\xi}_2$$

$$\dot{n}_{H,out} = \dot{\xi}_1 + \dot{\xi}_2$$

$$\dot{n}_{W,out} = \dot{n}_{W,in}$$

where EA = ethane, EE = ethylene, A = acetylene, H = hydrogen, and W = water (steam). Since this is a gas-phase reaction,

$$K_{a1} = \frac{y_{EE}y_H}{y_{EA}}P = \frac{(\dot{\xi}_1 - \dot{\xi}_2)(\dot{\xi}_1 + \dot{\xi}_2)}{(\dot{n}_{EA,in} - \dot{\xi}_1)(\dot{n}_{EA,in} + \dot{n}_{W,in} + \dot{\xi}_1 + \dot{\xi}_2)}P$$

$$K_{a2} = \frac{y_Ay_H}{y_{EE}}P = \frac{(\dot{\xi}_2)(\dot{\xi}_1 + \dot{\xi}_2)}{(\dot{\xi}_1 - \dot{\xi}_2)(\dot{n}_{EA,in} + \dot{n}_{W,in} + \dot{\xi}_1 + \dot{\xi}_2)}P$$

If we choose as a basis 100 gmol/h ethane fed to the reactor, we can examine first the case with 1:1 ethane:steam ratio, $T = 1000$ K, and $P = 1$ atm, $K_{a1} = 0.154$ and $K_{a2} = 0.00049$. We insert these values into the previous 2 equations and find $\dot{\xi}_1 = 45.4$ and $\dot{\xi}_2 = 0.12$ gmol/h. We then calculate yield and selectivity.

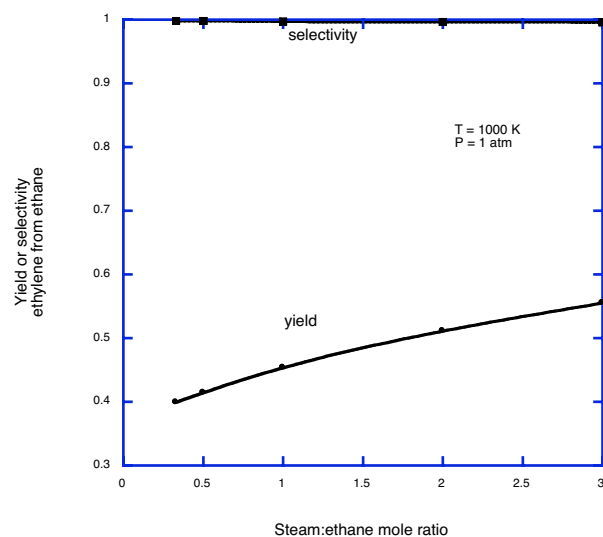
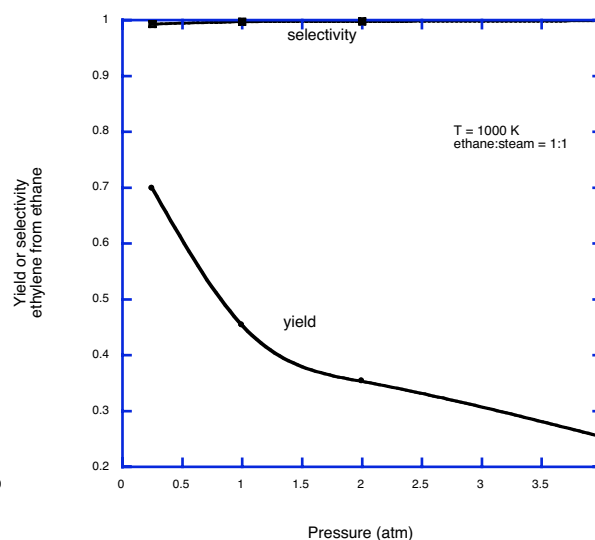
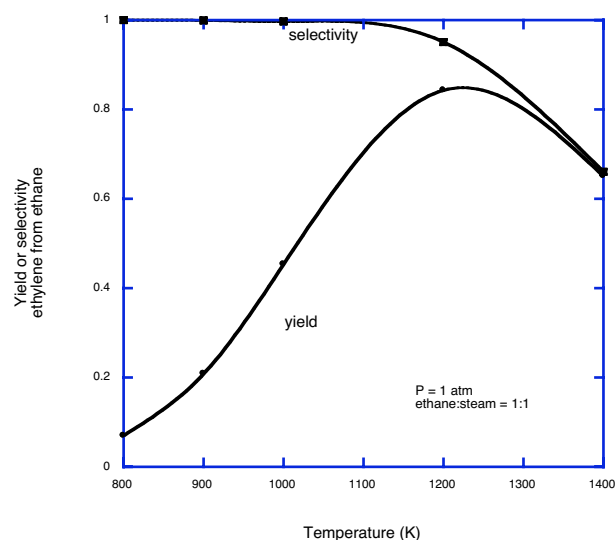
$$y_{EA \rightarrow EE} = \frac{\dot{\xi}_1 - \dot{\xi}_2}{\dot{n}_{E,in}} = \frac{45.4 - 0.12}{100} = 0.453$$

$$s_{EA \rightarrow EE} = \frac{\dot{\xi}_1 - \dot{\xi}_2}{\dot{\xi}_1} = \frac{45.4 - 0.12}{45.4} = 0.997$$

We use the same set of equations to examine trends in yield and selectivity with changing reactor temperature, pressure, or ethane:steam feed ratio. The ethane feed was kept constant at 100 gmol/h. Some results are summarized in the table and trends are plotted.

T (K)	P (atm)	Steam:ethane	K_{a1}	K_{a2}	$\dot{\xi}_1$	$\dot{\xi}_2$	$y_{EA \rightarrow EE}$	$s_{EA \rightarrow EE}$
1000	1	1:1	0.154	0.00049	45.4	0.12	0.453	0.997
800	1	1:1	0.00255	2.46e-6	7.01	0.0005	0.07	0.9999
900	1	1:1	0.0248	4.64e-5	20.85	0.0102	0.208	0.9995
1200	1	1:1	2.36	0.0164	88.66	4.36	0.843	0.951
1400	1	1:1	16.62	0.203	98.44	33.33	0.651	0.661
1000	0.25	1:1	0.154	0.00049	70.31	0.518	0.698	0.993
1000	2	1:1	0.154	0.00049	34.38	0.0567	0.353	0.998
1000	4	1:1	0.154	0.00049	25.415	0.0273	0.254	0.9989

1000	1	0.33:1	0.154	0.00049	39.96	0.0837	0.399	0.998
1000	1	0.5:1	0.154	0.00049	41.5	0.093	0.414	0.998
1000	1	2:1	0.154	0.00049	51.29	0.170	0.511	0.9967
1000	1	3:1	0.154	0.00049	55.71	0.22	0.555	0.996



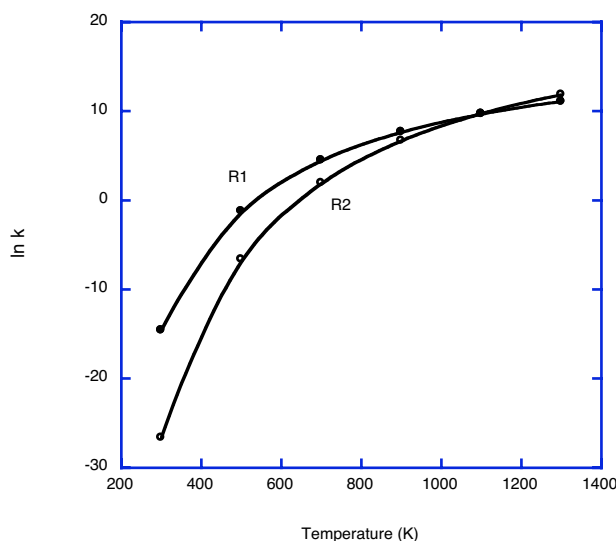
Increasing the temperature up to 1200 K improves yield but selectivity starts to drop. This is because equilibrium becomes more favorable with increasing temperature for both reactions, but the temperature effect is more pronounced in the second reaction. A temperature of around 1100 K provides a good balance between high yield and high selectivity. Increasing the pressure decreases yield but has little effect on selectivity, because pressure has similar effects on both reactions. Low pressure operation is desired, but operating at a vacuum is more expensive, and carries the risk of infiltration of air, so for both safety and economics it is preferable to operate no lower than atmospheric unless it can't be avoided. Increasing the steam:ethane ratio has a slight positive effect on yield without adversely affecting selectivity much. The disadvantage to

a high steam:ethane ratio is that (a) the reactor needs to be larger, and hence more expensive, to handle the higher total flow rates and (b) more steam must be separated out, increasing separation costs.

To summarize, I would choose: ~ 1100 K, 1 atm and 3:1 steam:ethane ratio (the latter subject to more study regarding the tradeoffs between higher yield and greater reactor and separator size).

P4.53

(R1) is the desired reaction. The rate constants for R1 and R2 are both functions of temperature, as shown.



(b) Selectivity is much better at lower temperatures. We would want to run the reactor at as low a temperature as feasible, to avoid generation of hazardous chlorinated byproducts. (We are assuming based on the information given that the reactions are under kinetic control, and not close to equilibrium.)

(a) I would feed with excess propylene, above the 2:1 propylene:chlorine stoichiometric ratio of (R1). The chlorinated byproducts are a hazardous waste. Furthermore, separating unreacted propylene from allyl chloride and HCl is relatively easy (as we will learn in Chapter 5), so the propylene could be recovered and recycled. This gives better overall selectivity and yield.

(c) The reaction rate constants have the same units, which indicates that the concentration dependence for the 2 reactions is the same. For gas-phase reactions, where the concentration is proportional to the pressure (see the ideal gas law), then we conclude that pressure changes would affect the two reaction rates equally.

P4.54

(1) 5% of the hydrogen peroxide decomposes in 24 h spontaneously by a first-order reaction. From equation (4.19) (which applies for a batch reactor and first-order irreversible kinetics) and the experimental data, we find the rate constant:

$$f_{CA} = 0.05 = 1 - e^{-kt_f} = 1 - e^{-k(24h)}$$

$$k = 0.00214 \text{ h}^{-1}$$

To get 99% conversion, then we set the fractional conversion to 0.99 and use the experimentally determined rate constant to find the required time:

$$f_{CA} = 0.99 = 1 - e^{-kt_f} = 1 - e^{-0.00214t_f}$$

$$t_f = 2152 \text{ h}$$

This is about 3 months!

(2) With the catalyst, the rate of decomposition is 0.0005 gmol/L-min, and is independent of the concentration in the reactor. Following the general development on p. 325, but adapting to the case where the rate is independent of concentration:

$$r_A' = \frac{dc_A}{dt} = -0.0005 \text{ gmol/L} \cdot \text{min}$$

Rearranging and integrating gives

$$\int_{c_{A0}}^{c_{Af}} dc_A = - \int_0^{t_f} 0.0005 dt$$

$$c_{Af} - c_{A0} = -0.0005t_f$$

where t_f is in minutes and c_{Af} is in gmol/L. The initial concentration in these units is

$$c_{A0} = \frac{3 \text{ g H}_2\text{O}_2}{1000 \text{ g solution}} \times \frac{1000 \text{ g solution}}{\text{L solution}} \times \frac{\text{gmol H}_2\text{O}_2}{34 \text{ g H}_2\text{O}_2} = 0.08824 \text{ gmol/L}$$

We want this to decrease to $(1 - 0.99)(0.08824) = 0.0008824 \text{ gmol/L} = c_{Af}$. Inserting these values into the equation above we find

$$0.0008824 - 0.08824 = -0.0005t_f$$

$$t_f = 175 \text{ minutes}$$

or about 3 hours!

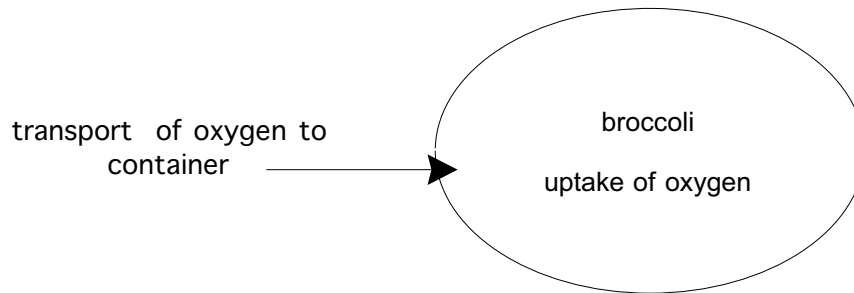
P4.55

The mole fraction of oxygen in the air is initially 0.21. Therefore, the initial rate of oxygen uptake is

$$\frac{219(0.21)}{0.014 + 0.21} = 205.3 \text{ mL O}_2/\text{kg broccoli/h}$$

Or, since there are 137 g broccoli, the rate of uptake is 28.1 mL O₂/h.

Oxygen is transferred across the barrier into the container at the same time as the oxygen uptake is occurring inside the container:



To state this in material balance terms:

$$In - Consumption = Accumulation$$

At steady-state, accumulation = 0, so $In = Consumption$ or

$$\dot{n}_{O_2,in} = \dot{r}_{O_2}$$

At steady state the mole fraction of oxygen in the container is 0.008. Therefore:

$$\dot{n}_{O_2,in} = \frac{219(0.008)}{0.014 + 0.008} \times 0.137 = 10.9 \text{ mL/h}$$