

Reading Question 9.1:

- a. The rate will increase. As temperature increases, the fraction of molecules having the energy needed to react goes up.
- b. The rate will increase. As pressure increases, the rate will increase.
- c. The rate will increase. The catalyst lowers the energy required for reaction and thereby increases the rate.

Reading Question 9.2:

One possibility is to increase the temperature of the reaction. This will increase the rate of reaction and allow the same output concentrations from a smaller reactor. Another possibility would be to use a catalyst, if one were available.

Reading Question 9.3:

The different results at the two locations without the mixer indicate that the system is not well mixed. Therefore, the system behavior should improve with the addition of the mixer.

Homework Problem 9.1:

The units of the pertinent variables are

$$r_{reaction} [=] \text{ moles/vol time}$$

$$c_A [=] \text{ moles/vol}$$

$$c_B [=] \text{ moles/vol}$$

Therefore, from the reaction rate equation,

$$r_{reaction} = k_r c_A^n c_B^m$$

Solving for k_r and applying the units,

$$k_r = \frac{r_{reaction}}{c_A^n c_B^m} [=] \frac{\text{ moles/vol time}}{(\text{ moles/vol})^n (\text{ moles/vol})^m}$$

$$[=] (\text{ moles})^{1-n-m} (\text{ vol})^{n+m-1} (\text{ time})^{-1}$$

Homework Problem 9.2:

Using *atmospheres* to represent any units of pressure, the units of the pertinent variables are

$$r_{reaction} [=] atm/time$$

$$p_A [=] atm$$

$$p_B [=] atm$$

Therefore, from the reaction rate equation,

$$r_{reaction} = k_r p_A^n p_B^m$$

Solving for k_r and applying the units,

$$k_r = \frac{r_{reaction}}{p_A^n p_B^m} [=] \frac{atm/time}{(atm)^n (atm)^m}$$

$$[=] (atm)^{1-n-m} (time)^{-1}$$

Homework Problem 9.3:

We need the reaction rate, which can be determined from the rate equation, which is

$$r_{reaction, sulfuric\ acid} = k_r C_{sulfuric\ acid} C_{diethyl\ ether}$$

Substituting the given values,

$$\begin{aligned} r_{reaction, sulfuric\ acid} &= (6.74 \times 10^{-4} \text{ L/gmol s})(0.53 \text{ gmol/L})(0.28 \text{ gmol/L}) \\ &= 0.00010 \text{ gmol/L s} \end{aligned}$$

Homework Problem 9.4:

- a. Since NO is the only reactant,

$$r_{reaction,NO} = k_r P_{NO}^n$$

Substituting the given units

$$\frac{gmol}{Ls} [=] \frac{gmol}{Ls (atm)^2} (atm)^n$$

from which we quickly deduce that $n = 2$, or the reaction is second order in NO.

- b. Re-writing the reaction equation with $n=2$,

$$r_{reaction,NO} = k_r P_{NO}^2$$

We can then solve for p_{NO} ,

$$P_{NO} = \sqrt{\frac{r_{reaction,NO}}{k_r}}$$

Substituting the given values into the equation

$$P_{NO} = \sqrt{\frac{0.056 gmol/min L}{0.0108 gmol/Ls atm^2} \left(\frac{1 min}{60 s}\right)} = 0.29 atm$$

$$= 4.3 psi = 3.0 \times 10^4 Pa$$

Homework Problem 9.5:

For the temperature of 5°C (which is 278 K),

$$k_r = k_0 e^{-E_d/RT}$$

$$= \left(5.2 \times 10^{13} \frac{L}{\text{gmol s}} \right) \exp \left\{ - \frac{3500 \text{ cal/gmol}}{\left(1.987 \frac{\text{cal}}{\text{gmol K}} \right) (278 \text{ K})} \right\} = 9.2 \times 10^{10} \frac{L}{\text{gmol s}}$$

Now the calculation on page 154 becomes

$$V = \frac{r_{\text{consumption,HCl}}}{k_r c_{\text{HCl}_{\text{out}}} c_{\text{NaOH}_{\text{out}}}}$$

$$= \frac{162 \text{ gmol/hr}}{\left(9.2 \times 10^{10} \frac{L}{\text{gmol s}} \right) \left(3.16 \times 10^{-7} \frac{\text{gmol}}{L} \right) \left(3.16 \times 10^{-7} \frac{\text{gmol}}{L} \right)} \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) = 4.9 \text{ L}$$

Homework Problem 9.6:

The diagram for this problem was already given. In order to determine the reactor volume, we will use the equation,

$$r_{cons,G} = r_{react,G} V = k_r c_G^2 V$$

The concentration in the equation is for conditions inside the reactor, but you remember that for a CSTR, the concentrations in the outlet stream are the same as those inside the reactor. In this case, the concentration of G in the outlet stream is given. Thus, we simply need to determine the consumption rate of G.

Mole balance on G: $\dot{n}_{G,in} = \dot{n}_{G,out} + r_{cons,G} V$

Because of the information which is given, this is more conveniently written

$$c_{G,in} \dot{V}_{G-stream} = c_{G,out} \dot{V}_{out} + r_{cons,G} V \quad (1)$$

Balance on Total Mass: $\dot{m}_{G-stream} + \dot{m}_{J-stream} = \dot{m}_{out}$

Again, because of the information which is given, this is more conveniently written

$$\rho_{G-stream} \dot{V}_{J-stream} + \rho_{J-stream} \dot{V}_{G-stream} = \rho_{out} \dot{V}_{out}$$

but all the densities are equal, so

$$\dot{V}_{J-stream} + \dot{V}_{G-stream} = \dot{V}_{out} \quad (2)$$

We could also write a mole balance on J and could write the stoichiometric relationship, but it turns out that these are not necessary and would not be helpful. The only other thing we need is to write the relationship given about the flow rate of the J stream:

$$\dot{V}_{J-stream} = 0.75 \dot{V}_{G-stream} \quad (3)$$

Solving these three equations,

From Equation 3, $\dot{V}_{J-stream} = 0.75(33 \text{ L/min}) = 25 \text{ L/min}$

From Equation 2, $\dot{V}_{out} = 33 \text{ L/min} + 25 \text{ L/min} = 58 \text{ L/min}$

From Equation 1, $r_{cons,G} = c_{G,in} \dot{V}_{G-stream} - c_{G,out} \dot{V}_{out}$

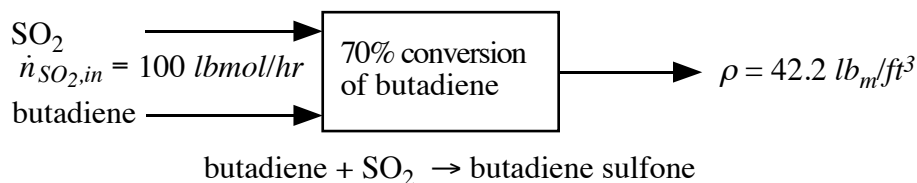
$$= \left(0.19 \frac{\text{gmol}}{\text{L}}\right) \left(33 \frac{\text{L}}{\text{min}}\right) - \left(0.04 \frac{\text{gmol}}{\text{L}}\right) \left(58 \frac{\text{L}}{\text{min}}\right) = 4.0 \frac{\text{gmol}}{\text{min}}$$

So,

$$V = \frac{r_{cons,G}}{r_{react,G}} = \frac{r_{cons,G}}{k_r c_{G,out}^2} = \frac{4.0 \text{ gmol/min}}{(1.8 \text{ L/gmol min})(.04 \text{ gmol/L})^2} = 1375 \text{ L}$$

Homework Problem 9.7:

- a. The diagram for this problem is



In order to determine the reactor volume, we will use the equation,

$$r_{cons, but} = r_{react, but} \cdot V = k_r c_{SO_2} c_{but} \cdot V$$

The concentrations in the equation are for conditions inside the reactor, but you remember that for a CSTR, the concentrations in the outlet stream are the same as those inside the reactor. So we will need to determine the outlet concentrations of SO₂ and butadiene. Furthermore, the outlet concentrations are related to the outlet molar flow rates as expressed by Equation 9.11.

$$c_A = \frac{\dot{n}_A}{\dot{V}}$$

so we actually will need to determine the molar flow rates of SO₂ and butadiene and the volume flow rate of the outlet stream.

Mole balance on SO₂:

$$\dot{n}_{SO_2, in} = \dot{n}_{SO_2, out} + r_{cons, SO_2} \quad (1)$$

(We could express the outlet molar flow rate in terms of concentration and volumetric flow rate, but in this problem, because of some of the given information, it is easier to work with molar flow rates until the end.)

Mole balance on butadiene:

$$\dot{n}_{but, in} = \dot{n}_{but, out} + r_{cons, but} \quad (2)$$

Balance on total mass:

$$\dot{m}_{SO_2, in} + \dot{m}_{but, in} = \dot{m}_{out}$$

In this case, it is more convenient to express these mass flow rates as follows:

$$MW_{SO_2} \dot{n}_{SO_2, in} + MW_{but} \dot{n}_{but, in} = \rho_{out} \dot{V}_{out} \quad (3)$$

where

$$MW_{SO_2} = 32.1 + 2(16.0) = 64.1$$

Stoichiometry:

$$\frac{r_{cons, SO_2}}{r_{cons, but}} = 1 \quad (4)$$

Conversion:

$$r_{cons, but} = 0.70 \dot{n}_{but, in} \quad (5)$$

Other (given information about the inlet flow rate of butadiene):

$$\dot{n}_{but, in} = 1.25 \dot{n}_{SO_2, in} \quad (6)$$

Homework Problem 9.7 (continued):

Now we can solve this equation set to determine the outlet molar flow rates of SO_2 and butadiene and the outlet volumetric flow rate.

$$\text{From Equation 6, } \dot{n}_{but.,in} = 1.25 \left(100 \frac{\text{lbmol}}{\text{hr}} \right) = 125 \frac{\text{lbmol}}{\text{hr}}$$

$$\text{From Equation 5, } r_{cons.,but.} = 0.70 \left(125 \frac{\text{lbmol}}{\text{hr}} \right) = 87.5 \frac{\text{lbmol}}{\text{hr}}$$

$$\text{From Equation 2, } \dot{n}_{but.,out} = \dot{n}_{but.,in} - r_{cons.,but.} = 125 \frac{\text{lbmol}}{\text{hr}} - 87.5 \frac{\text{lbmol}}{\text{hr}} = 37.5 \frac{\text{lbmol}}{\text{hr}}$$

$$\text{From Equation 4, } r_{cons.,SO_2} = r_{cons.,but.} = 87.5 \frac{\text{lbmol}}{\text{hr}}$$

$$\text{From Equation 1, } \dot{n}_{SO_2,out} = \dot{n}_{SO_2,in} - r_{cons.,SO_2} = 100 \frac{\text{lbmol}}{\text{hr}} - 87.5 \frac{\text{lbmol}}{\text{hr}} = 12.5 \frac{\text{lbmol}}{\text{hr}}$$

$$\begin{aligned} \text{From Equation 3: } \dot{V}_{out} &= \frac{MW_{SO_2} \dot{n}_{SO_2,in} + MW_{but} \dot{n}_{but.,in}}{\rho_{out}} \\ &= \frac{\left(64.1 \frac{\text{lb}_m}{\text{lbmol}} \right) \left(100 \frac{\text{lbmol}}{\text{hr}} \right) + \left(54 \frac{\text{lb}_m}{\text{lbmol}} \right) \left(125 \frac{\text{lbmol}}{\text{hr}} \right)}{42.2 \frac{\text{lb}_m}{\text{ft}^3}} \\ &= 312 \text{ ft}^3/\text{hr} \end{aligned}$$

$$\text{So } c_{SO_2,out} = \frac{\dot{n}_{SO_2,out}}{\dot{V}_{out}} = \frac{12.5 \text{ lbmol/hr}}{312 \text{ ft}^3/\text{hr}} = 0.040 \frac{\text{lbmol}}{\text{ft}^3}$$

$$\text{and } c_{but.,out} = \frac{\dot{n}_{but.,out}}{\dot{V}_{out}} = \frac{37.5 \text{ lbmol/hr}}{312 \text{ ft}^3/\text{hr}} = 0.120 \frac{\text{lbmol}}{\text{ft}^3}$$

Finally, we can now determine the reaction rate, which is

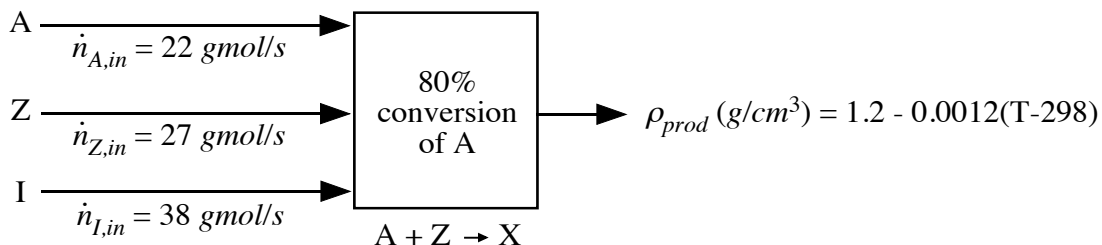
$$\begin{aligned} r_{react.,but.} &= k_r c_{SO_2} c_{but.} \\ &= \left(4.44 \frac{\text{ft}^3}{\text{lbmol hr}} \right) \left(.040 \frac{\text{lbmol}}{\text{ft}^3} \right) \left(.120 \frac{\text{lbmol}}{\text{ft}^3} \right) = .0213 \frac{\text{lbmol}}{\text{ft}^3 \text{ hr}} \end{aligned}$$

And the reactor volume is

$$V = \frac{r_{cons.,but.}}{r_{react.,but.}} = \frac{87.5 \text{ lbmol/hr}}{.0213 \text{ lbmol/ft}^3 \text{ hr}} = 4100 \text{ ft}^3$$

- b. The addition of an inert liquid to the butadiene feed would dilute the contents of the reactor, so the concentrations in the reactor would be lower. As a result, the reaction would proceed more slowly, and a larger reactor would be needed to produce the same conversion of butadiene.

Homework Problem 9.8: The diagram for this problem is



Before we construct the spreadsheet solution, we need to set up the strategy. We begin by writing the appropriate balances as with all such problems.

In order to determine the reactor volume, we will use the equation,

$$r_{cons,A} = r_{react,A} V = k_r c_A c_Z V$$

The concentrations in the equation are for conditions inside the reactor, but you remember that for a CSTR, the concentrations in the outlet stream are the same as those inside the reactor. So we will need to determine the concentrations of A and Z in the product stream.

Mole balance on A:

$$\dot{n}_{A,in} = \dot{n}_{A,out} + r_{cons,A} V$$

But this would be more conveniently written

$$\dot{n}_{A,in} = c_{A,out} \dot{V}_{prod} + r_{cons,A} V \quad (1)$$

Mole balance on Z:

$$\dot{n}_{Z,in} = \dot{n}_{Z,out} + r_{cons,Z} V$$

which, again, would be more conveniently written

$$\dot{n}_{Z,in} = c_{Z,out} \dot{V}_{prod} + r_{cons,Z} V \quad (2)$$

Balance on total mass:

$$\dot{m}_A + \dot{m}_Z + \dot{m}_I = \dot{m}_{prod}$$

Because of the given molecular weights and formula for density, this equation is more conveniently written

$$MW_A \dot{n}_{A,in} + MW_Z \dot{n}_{Z,in} + MW_I \dot{n}_{I,in} = \rho_{prod} \dot{V}_{prod} \quad (3)$$

Stoichiometry:

$$\frac{r_{cons,Z}}{r_{cons,A}} = 1 \quad (4)$$

Conversion:

$$r_{cons,A} = 0.80 \dot{n}_{A,in} \quad (5)$$

Finally, we rearrange the reaction equation written above to give

$$V = \frac{r_{cons,A}}{r_{react,A}} = \frac{r_{cons,A}}{k_r c_{A,out} c_{Z,out}} = \frac{r_{cons,A}}{k_0 e^{-E_a/RT} c_{A,out} c_{Z,out}} \quad (6)$$

Some of the values can be determined immediately as follows:

From Equation 5, $r_{cons,A} = 0.80(22 \text{ gmol/s}) = 17.6 \text{ gmol/s}$

From Equation 4, $r_{cons,Z} = r_{cons,A} = 17.6 \text{ gmol/s}$

Homework Problem 9.8 (continued):

The rest of the strategy is established by rearranging the mole and mass balances:

$$\text{From Equation 3, } \dot{V}_{prod} = \frac{MW_A \dot{n}_{A,in} + MW_Z \dot{n}_{Z,in} + MW_I \dot{n}_{I,in}}{\rho_{prod}}$$

$$\text{From Equation 1, } c_{A,out} = \frac{\dot{n}_{A,in} - r_{cons,A}}{\dot{V}_{prod}}$$

$$\text{From Equation 2, } c_{Z,out} = \frac{\dot{n}_{Z,in} - r_{cons,Z}}{\dot{V}_{prod}}$$

So the spreadsheet strategy will be that, for each temperature,

1. calculate $k_r = k_0 e^{-E_a/RT}$
 2. calculate ρ_{prod} with given relation
 3. calculate \dot{V}_{prod} as shown above (divide by 1000 to convert cm^3/s to *Liters/s*)
 4. calculate $c_{A,out}$ as shown above
 5. calculate $c_{Z,out}$ as shown above
 6. calculate $r_{react,A} = k_r c_A c_Z$
 7. calculate reactor volume (Equation 6)
- a. The spreadsheet with these calculations is shown here.

T (K)	kr (L/gmol s)	rho (g/cm ³)	Vol flow (L/s)	cA,out gmol/L	cZ,out gmol/L	reaction rate (gmol/L s)	Vreactor (L)
298	1.575E-07	1.200	4.372	1.006	2.150	3.409E-07	51624222
300	2.246E-07	1.198	4.380	1.004	2.146	4.841E-07	36355327
305	5.341E-07	1.192	4.402	0.999	2.135	1.140E-06	15442128
310	1.235E-06	1.186	4.425	0.994	2.124	2.609E-06	6745350
315	2.781E-06	1.180	4.447	0.989	2.114	5.816E-06	3026094
320	6.106E-06	1.174	4.470	0.984	2.103	1.264E-05	1392513
325	1.308E-05	1.168	4.493	0.979	2.092	2.681E-05	656519
330	2.740E-05	1.162	4.516	0.974	2.081	5.556E-05	316773
335	5.612E-05	1.156	4.540	0.969	2.071	1.126E-04	156262
340	1.126E-04	1.150	4.563	0.964	2.060	2.235E-04	78730
345	2.212E-04	1.144	4.587	0.959	2.049	4.348E-04	40477
350	4.265E-04	1.138	4.611	0.954	2.038	8.295E-04	21217
355	8.072E-04	1.132	4.636	0.949	2.028	1.553E-03	11330
360	1.501E-03	1.126	4.661	0.944	2.017	2.858E-03	6159
365	2.744E-03	1.120	4.686	0.939	2.006	5.169E-03	3405
370	4.934E-03	1.114	4.711	0.934	1.995	9.196E-03	1914
375	8.736E-03	1.108	4.736	0.929	1.985	1.611E-02	1093
380	1.524E-02	1.102	4.762	0.924	1.974	2.779E-02	633

Homework Problem 9.8 (continued):

- b. The required reactor volume decreased with increasing temperature. This happens because higher temperatures produce a faster reaction rate constant and reaction rate. Thus, less reaction time and a smaller reactor are needed.
- c. In the given temperature range, the highest temperature (375 K) is recommended, because it requires the smallest reactor (1093 L).
- d. At room temperature (298 K), the required reactor volume is more than 51 million liters. This clearly is infeasible.
- e. Operating at high temperatures, such as 375 K as recommended in part c, involves the following challenges:
 - Maintaining the elevated reactor temperature will involve heating costs, which may influence the choice of temperature.
 - The elevated temperature may produce additional corrosion and other degradation of the equipment. Special materials may be needed to reduce that degradation, and those materials will involve additional costs. Alternately, the equipment may need to be replaced more frequently, and that more frequent replacement will entail greater costs.