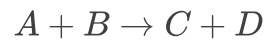


## Problem 5-11

---

Reaction (gas-phase, elementary, irreversible):



PBR, isothermal.

$$T = 305K, W = 100kg, P_0 = 20atm, P = 2atm, F_{A0} = F_{B0} = 10 \frac{mol}{min}, C_{A0} = 0.4 \frac{mol}{L}$$

$$X = 0.8$$

What would be  $X'$  if catalyst particle size were doubled?

Ergun equation:

$$\frac{dP}{dz} = -\beta \frac{P_0 T F_T}{P T_0 F_{T0}}$$

$$X' = \frac{\beta}{\beta'} X$$

With  $\epsilon = 0$ :

$$\beta = \frac{R_e}{\rho_0 g_c D_p} \left( \frac{1 - \phi}{\phi^3} \right) \left[ \frac{150(1 - \phi)\mu}{D_p} + 1.75 R_e \right]$$

Doubling the catalyst particle diameter:

$$\beta' = \frac{R_e}{2\rho_0 g_c D_p} \left( \frac{1 - \phi}{\phi^3} \right) \left[ \frac{150(1 - \phi)\mu}{2D_p} + 1.75 R_e \right]$$

Taking the ratio and multiplying top and bottom by  $D_p$ :

$$\frac{\beta}{\beta'} = \frac{1}{2} \frac{150(1 - \phi)\mu + 1.75 R_e D_p}{75(1 - \phi)\mu + 1.75 R_e D_p}$$

For turbulent flow,  $R_e \geq 3500$ , and for a gas-phase reaction,  $\mu \approx 10^{-5}$ . Therefore:

$$\frac{\beta}{\beta'} \approx \frac{1}{2} \frac{0 + 1.75 R_e D_p}{0 + 1.75 R_e D_p}$$

$$X = \frac{1}{2} X' = 0.4$$

## Problem 5-13

Wouldn't it be much easier to sabotage the methylamine by adding bleach? Just a thought.

Chemical reaction:  $2A \rightleftharpoons B + C$

Gas-phase, elementary rate law.

$$k_1 = 4.25 * 10^{-6} \frac{\text{mol}}{\text{atm}^2 \text{g}_{\text{cat}} \text{s}} \text{ and } K_e = 2.5$$

Inlet conditions  $F_{A0} = 23.6 \frac{\text{mol}}{\text{s}}$  and  $P_0 = 18 \text{atm}$

Initially, assume no pressure drop or temperature change across the reactor.

**(a)**

Write the mole balance.

$$\frac{dC_A}{dW} = -2 \frac{dC_B}{dW} = -2 \frac{dC_C}{dW}$$

or

$$\frac{dP_A}{dW} = -2 \frac{dP_B}{dW} = -2 \frac{dP_C}{dW}$$

and

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$$

**(b)**

Write the rate law in terms of partial pressures.

$$-r_A = k_1 P_A^2 - k_2 P_B P_C$$

$$k_2 = \frac{k_1}{K_e}$$

$$P_B = P_C$$

$$-r_A = k_1 \left( P_A^2 - \frac{P_B^2}{K_e} \right)$$

**(c)**

Set up a stoichiometric table for this reaction.

	Species	Symbol	Initial	Change	Net
<b>1</b>	<i>methylamine</i>	<i>A</i>	$N_{A0}$	$-XN_{A0}$	$N_A = N_{A0}(1 - X)$
<b>2</b>	<i>dimethylamine</i>	<i>B</i>	$N_{B0} = 0$	$\frac{1}{2}XN_{A0}$	$N_B = \frac{1}{2}XN_{A0}$
<b>3</b>	<i>ammonia</i>	<i>C</i>	$N_{C0} = 0$	$\frac{1}{2}XN_{A0}$	$N_C = \frac{1}{2}XN_{A0}$

**(d)**

Write the partial pressures in terms of conversion.

$$P_A = P_0(1 - X)$$

$$P_B = P_C = \frac{1}{2}XP_0$$

**(e)**

Write the rate law solely in terms of conversion.

$$-r_A = k_1 \left( P_A^2 - \frac{P_B^2}{K_e} \right)$$

$$-r_A = k_1 \left( (P_0(1 - X))^2 - \frac{(\frac{1}{2}XP_0)^2}{K_e} \right)$$

$$-r_A = k_1 P_0^2 \left( 1 - 2X + X^2 \left( 1 - \frac{1}{4K_e} \right) \right)$$

**(f)**

What is the equilibrium conversion  $X_e$ ?

$$-r_A = k_1 P_0^2 \left( 1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right) \right) = 0$$

$$\left( 1 - \frac{1}{4K_e} \right) X_e^2 - 2X_e + 1 = 0$$

Solving the quadratic and taking the physical root (i.e.  $X \leq 1$ ):

The roots are 1.4624752955742644 and 0.7597469266479578

```
. begin
.   # set up coefficients
.   Ke = 2.5
.   local a = 1 - 0.25 / Ke
.   local b = -2
.   local c = 1
.   # solve quadratic
.   X_partf = 0.5 .* (-b .+ [1, -1] .* sqrt(b^2 - 4*a*c)) ./ a
.   # record roots for subsequent parts
.   p, q = X_partf
.
.   md"The roots are $p and $q"
. end
```

The conversion is 0.7597

```
. begin
.   # take the root that is within [0, 1]
.   local X = X_partf
.   Xe = round(X[X ≤ 1][1], digits=4)
.
.   md"The conversion is $Xe"
. end
```

(g)

Write out your algorithm in terms of conversion.

I think this means: express  $W$  in terms of  $X$  (or vice-versa).

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$$

$$\frac{dX}{dW} = \frac{k_1 P_0^2}{F_{A0}} \left( 1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right) \right) \left( \frac{P}{P_0} \right)^2$$

$$\frac{P}{P_0} = 1$$

$$dW = \frac{F_{A0}}{k_1 P_0^2} \frac{dX}{1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right)}$$

$$\int dW = \frac{F_{A0}}{k_1 P_0^2} \int \frac{dX}{1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right)}$$

$p, q \equiv$  quadratic roots from previous part. Applying the integral formula from Fogler (A-11):

$$W = \frac{F_{A0}}{k_1 P_0^2} \frac{1}{\left( 1 - \frac{1}{4K_e} \right) (p - q)} \ln \left( \frac{q(X - p)}{p(X - q)} \right)$$

(h)

How much catalyst is needed in a PBR to obtain 75 % and 90 % of equilibrium conversion?

```
• begin
•   # set up coefficients
•   P0 = 18 # atm
•   Fa0 = 23.6 # mol/s
•   k1 = 4.25e-6 # mol/atm2/g_cat/s
•
•   # weight expression
•   W_PBR(X) =
•       Fa0 * log(q * (X - p) / p / (X - q)) / k1 / P02 / (1 - 1 / 4 / Ke) / (p - q)
• end;
```

The catalyst weight to achieve 75 % of equilibrium conversion is 24.2 kg

```
• begin
•   # solve for  $X = 0.75X_e$ 
•   local  $W_x = W\_PBR(0.75 * X_e)$ 
•   # convert to kg and round
•   local  $W_x = round(W_x / 1e3, digits=1)$ 
•   md"The catalyst weight to achieve 75 % of equilibrium conversion is  $W_x$  kg"
• end
```

The catalyst weight to achieve 90 % of equilibrium conversion is 45.3 kg

```
• begin
•   # solve for  $X = 0.9X_e$ 
•   local  $W_x = W\_PBR(0.9 * X_e)$ 
•   # convert to kg and round
•   local  $W_x = round(W_x / 1e3, digits=1)$ 
•   md"The catalyst weight to achieve 90 % of equilibrium conversion is  $W_x$  kg"
• end
```

**(i)**

How much catalyst would be needed to obtain 90 % of equilibrium conversion in a fluidized-bed reactor? How can the weight be reduced?

Fluidized-bed reactor performance equation:

$$W = \frac{F_{A0}X}{-r_A}$$

Catalyst weight expression:

$$W = \frac{F_{A0}X}{k_1 P_0^2 \left( 1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right) \right)}$$

The mass of catalyst is 395 tonnes (which would cost in the neighborhood of 10M USD!)

To reduce the required mass (without changing reactor type), either the inlet pressure must be increased or the molar flow rate decreased.

```

• begin
•   # weight expression
•   W_FBR(X) = FA0 * X / k1 / P02 / (1 - 2 * Xe + Xe2 * (1 - 1 / 4 / Ke))
•   # solve for the catalyst weight
•   local Wx = W_FBR(0.9 * Xe)
•   # convert to tonnes and round
•   local Wx = Int(round(Wx / 1e6, digits=0))
•
• md"
• The mass of catalyst is $Wx tonnes (which would cost in the neighborhood of 10M USD!)
•
• To reduce the required mass (without changing reactor type), either the inlet
  pressure must be increased or the molar flow rate decreased.
• "
• end

```

(j)

What conversion is achieved in a 100 kg PBR, accounting for pressure drop with  $\alpha = 0.0098 \text{ kg}^{-1}$ ?

What mass of catalyst is needed to keep the exit pressure  $\geq 1 \text{ atm}$ ?

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$$

$$\frac{dX}{dW} = \frac{k_1 P_0^2}{F_{A0}} \left( 1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right) \right) \left( \frac{P}{P_0} \right)^2$$

$$\frac{P}{P_0} = \sqrt{1 - \alpha W}$$

$$\int (1 - \alpha W) dW = \frac{F_{A0}}{k_1 P_0^2} \int \frac{dX}{1 - 2X_e + X_e^2 \left( 1 - \frac{1}{4K_e} \right)}$$

$$W - \frac{\alpha}{2} W^2 = \frac{F_{A0}}{k_1 P_0^2} \frac{1}{\left( 1 - \frac{1}{4K_e} \right) (p - q)} \ln \left( \frac{q(X - p)}{p(X - q)} \right)$$



```

• begin
•   # set weight
•   W = 100 # kg
•   # left- and right-hand terms of above expression
•   lefthand_term(α) = W - α * W^2 / 2
•   righthand_term(X) =
•       Fa0 * log(q * (X - p) / p / (X - q)) / k1 / P0^2 / (1 - 1 / 4 / Ke) / (p - q)
• end;

```

```

• function X_with_P_drop(α)
•   # calculate the left-hand term
•   L = lefthand_term(α)
•   # calculate the right-hand term over the interval X ∈ [0, 1]
•   X_range = Complex.(0:0.01:1) # complex nums to avoid log(x < 0) errors
•   R = righthand_term(X_range)
•   # find the index of the X value giving the minimum error between L and R
•   i = argmin(abs.(R .- L))
•   # get the corresponding X value
•   return real(X_range[i])
• end;

```

The calculation above gives a conversion of 0.0

This does not seem correct...

```

• begin
•   local X = X_with_P_drop(0.0098)
•   md"
•   The calculation above gives a conversion of $X
•
•   This does not seem correct...
•   "
• end

```

$$\frac{P}{P_0} = \sqrt{1 - \alpha W}$$

Catalyst weight to achieve a specific outlet pressure:

$$W = \frac{1}{\alpha} \left( 1 - \frac{P^2}{P_0^2} \right)$$

```

• W_for_P_out(P, α) = (1 - P^2 / P0^2) / α;

```

To maintain atmospheric pressure at the outlet of the reactor, no more than 101.7 kg of catalyst may be used.

```
• begin
•   # calculate catalyst weight for given P, α
•   local W = W_for_P_out(1, 0.0098)
•   # round
•   local W = round(W, digits=1)
• md"
• To maintain atmospheric pressure at the outlet of the reactor, no more than $W kg of
• catalyst may be used.
• "
• end
```

(k)

Repeat (j) with  $\alpha = 6 * 10^{-4}$

The conversion calculated is 0.01

Again, this result is suspiciously tiny...

```
• begin
•   local X = X_with_P_drop(6e-4)
• md"
• The conversion calculated is $X
•
• Again, this result is suspiciously tiny...
• "
• end
```

To maintain atmospheric pressure at the outlet of the reactor, no more than 1662 kg of catalyst may be used.

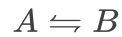
```
• begin
•   local W = W_for_P_out(1, 6e-4)
•   W = Int(round(W, digits=0))
• md"
• To maintain atmospheric pressure at the outlet of the reactor, no more than $W kg of
• catalyst may be used.
• "
• end
```



## Problem 11-2

---

Elementary reaction:



$$X_e = 0.8 \text{ at } T = 127^\circ\text{C}$$

$$X_e = 0.5 \text{ at } T = 227^\circ\text{C}$$

What is  $\Delta H^\circ$ ?

$$T_1 = 400\text{K}$$

$$T_2 = 500\text{K}$$

Van't Hoff equation:

$$\frac{d}{dT} \ln K_{eq} = \frac{\Delta H^\circ}{RT^2}$$

$$K_{eq} = \exp\left(\frac{3\Delta H^\circ T^3}{R}\right)$$

$$\frac{0.8}{0.5} = \exp\left(\frac{3\Delta H^\circ(400^3 - 500^3)}{R}\right)$$

$$\Delta H^\circ = \frac{\frac{R}{3} \ln\left(\frac{0.8}{0.5}\right)}{400^3 - 500^3}$$

$$\Delta H^\circ = -5.103263449788398\text{e-}9$$

$$\bullet \Delta H^\circ = 1.987 * \log(0.8 / 0.5) / 3 / (400^3 - 500^3)$$

The enthalpy is -5.1e-9 cal/mol

