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.

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

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

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
1	*methylamine*	A	N_{A0}	$-X N_{A0}$	$N_A = N_{A0}(1 - X)$
2	*dimethylamine*	B	$N_{B0} = 0$	$\frac{1}{2} X N_{A0}$	$N_B = \frac{1}{2} X N_{A0}$
3	*ammonia*	C	$N_{C0} = 0$	$\frac{1}{2} X N_{A0}$	$N_C = \frac{1}{2} X N_{A0}$

(d)

Write the partial pressures in terms of conversion.

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

$$P_B = P_C = \frac{1}{2} X P_0$$

(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] .* √(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):

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

(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 / P₀^2 / (1 - 1 / 4 / Kₑ) / (p - q)
end;
```

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

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

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

```
• begin
•     # solve for X = 0.9Xₑ
•     local Wₓ = W_PBR(0.9 * Xₑ)
•     # convert to kg and round
•     local Wₓ = round(Wₓ / 1e3, digits=1)
•     md"The catalyst weight to achieve 90 % of equilibrium conversion is $Wₓ 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 / P₀^2 / (1 - 2 * Xₑ + Xₑ^2 * (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 $\alpha = 0.0098 kg^{-1}$?
What mass of catalyst is needed to keep the exit pressure $\geq$ 1 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) =
        F_{a0} * log(q * (X - p) / p / (X - q)) / k_1 / P_0^2 / (1 - 1 / 4 / K_e) / (p - q)
end;
```

```
function X_with_P_drop(α)
    # calcualte 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 / P_0^2) / 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
```