CHEN 364 HW8

May 2, 2023

[ ]:
```python
from numpy import linspace
from matplotlib.pyplot import plot, title, legend, grid, xlabel, ylabel, xticks, yticks
from scipy.integrate import solve_ivp
```

1 Problem 1

Write the rate law for each step.

$A + S \rightarrow A \cdot S$, rate: $R_{AA} = K_{AA}\left(P_A C_S - \frac{C_{AS}}{K_{AA}}\right)$

$A \cdot S + S \rightarrow B \cdot S + C \cdot S$, rate: $r_S = k_S\left(C_{AS} - \frac{C_{BS}C_{CS}}{K_S}\right)$

$B \cdot S \rightarrow B + S$, rate: $r_{DB} = k_{DB}\left(C_{BS} - \frac{P_B C_S}{K_{DB}}\right)$

$C \cdot S \rightarrow C + S$, rate: $r_{DC} = k_{DC}\left(C_{CS} - \frac{P_C C_S}{K_{DC}}\right)$

Substitute:

$C_{AS} = K_{AA} P_A C_S$

$C_{BS} = \frac{P_B C_S}{K_{DB}} = K_{AB} P_B C_S$

$C_{CS} = \frac{P_C C_S}{K_{DC}} = K_{AC} P_C C_S$

$r_S = k_S\left(K_{AA} P_A C_S^2 - \frac{P_B P_C C_S^2}{K_S K_{DB} K_{DC}}\right)$

$K_{eq} = K_S K_{AA} K_{DB} K_{DC}$

$r_S = k_S K_{AA} C_S^2\left(P_A - \frac{P_B P_C}{K_{eq}}\right)$

Site balance:

$C_T = C_S + C_{AS} + C_{BS} + C_{CS}$

$C_T = C_S + K_{AA} P_A C_S + \frac{P_B C_S}{K_{DB}} + \frac{P_C C_S}{K_{DC}}$

$C_S = \frac{C_T}{1 + K_{AA} P_A + K_{AB} P_B + K_{AC} P_C}$

$r = \frac{k_S K_{AA} C_T^2\left(P_A - \frac{P_B P_C}{K_{eq}}\right)}{(1 + K_{AA} P_A + K_{AB} P_B + K_{AC} P_C)^2}$

At initial conditions:

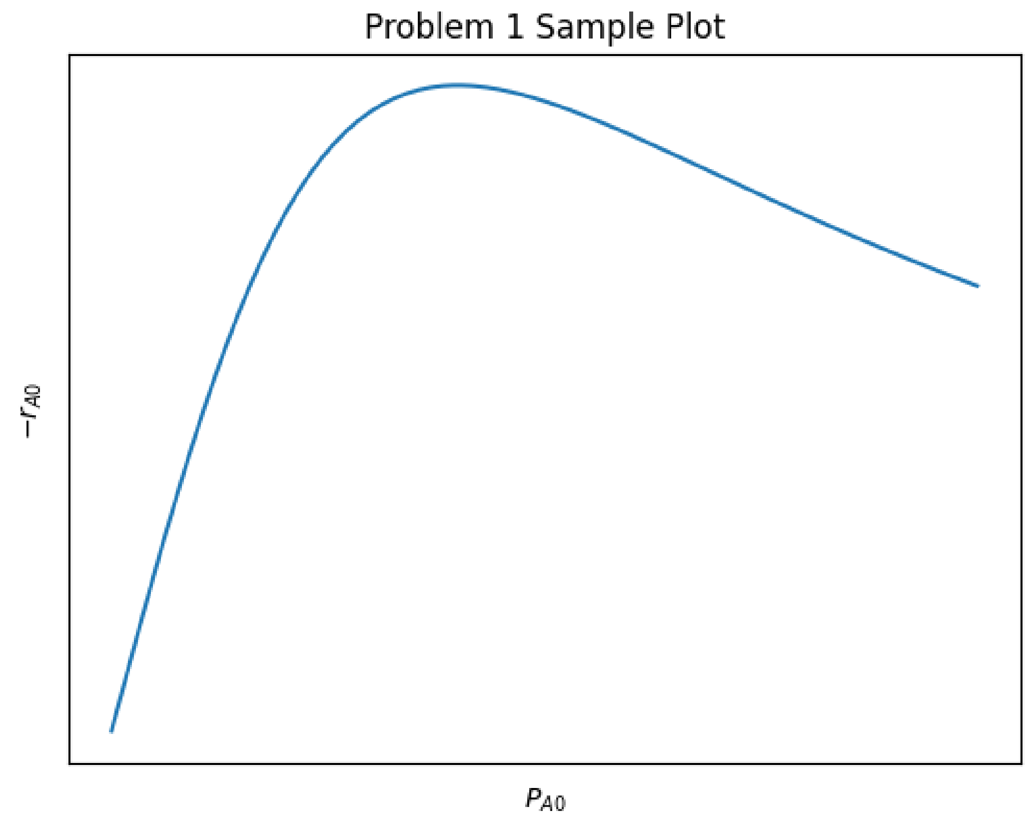
$P_{B0} = P_{C0} = 0$

$r = \frac{k_S K_{AA} C_T^2 P_{A0}}{(1+K_{AA}P_{A0})^2}$

[ ]:
```python
P = linspace(0, 2.5, 100)
r = lambda P: P / (1 + P**2)

plot(P, r(P))
xticks([])
yticks([])
xlabel(r"$P_{A0}$")
ylabel(r"$-r_{A0}$")
title("Problem 1 Sample Plot")
```

[ ]: Text(0.5, 1.0, 'Problem 1 Sample Plot')



The shape of the plot from the equation is the same as the experimental data. This relationship is consistent because at low values of P_{A0} the reaction rate is slow due to a low concentration of A. At high value of P_{A0}, there are a smaller number of catalytic sites available which limits the rate of the reaction, and so the reaction slows down.

2 Problem 2

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

$-r_{AS} = k' C_{AS}$

$W = k_c\left(C_A - C_{AS}\right)$

Assume the reaction is mass transfer limited.

$W = k' C_{AS}$

$k_c\left(C_A - C_{AS}\right) = k' C_{AS}$

$C_{AS} = \frac{k_c C_A}{k_c + k'}$

$-r_{AS} = \frac{k' k_c C_A}{k_c + k'}$

$\mathrm{Sh} = 100\mathrm{Re}^{1/2}$

$k_c = \frac{D_e \mathrm{Re}}{d_p}$

$k_c = \frac{D_e}{d_p} 100 \left(\frac{u d_p}{\upsilon}\right)^{1/2}$

$k_c = \frac{10^{-2}}{0.1} 100 \left(\frac{10 \cdot 0.1}{0.02}\right)^{1/2}$

$k_c = 70.7 \text{ cm/s}$

$k_c a = 70.7 \cdot 60$

$k_c = 4242.6 \text{ cm}^3/\text{g cat/s}$

$C_A = C_{A0}\left(\frac{1-X}{1-\epsilon X}\right)$

$\epsilon = 0$

$C_A = C_{A0}\left(1 - X\right)$

$-r_{AS} = \frac{k' k_c C_{A0}(1-X)}{k_c + k'}$

$k' = 0.01,\ C_{A0} = 1,\ F_{A0} = 10000$

$-r_{AS} = \frac{0.01 \cdot 4242(1-X)}{4242 + 0.01}$

$\frac{dX}{dW} = \frac{0.01 \cdot 4242(1-X)}{4242.01 \cdot 10000}$

Solve the differential equation.

[ ]:
```
k_c = 1e-2 / 0.1 * 100 * (10 * 0.1 / 0.02)**0.5 * 60
C_A0 = 1
r_A = lambda C_A: -0.01 * k_c * C_A / (4242 + 0.01)
C_A = lambda X: C_A0 * (1 - X)
F_A0 = 10000
p2_ode = lambda t, y: -r_A(C_A(y)) / F_A0

W = 916.16
```

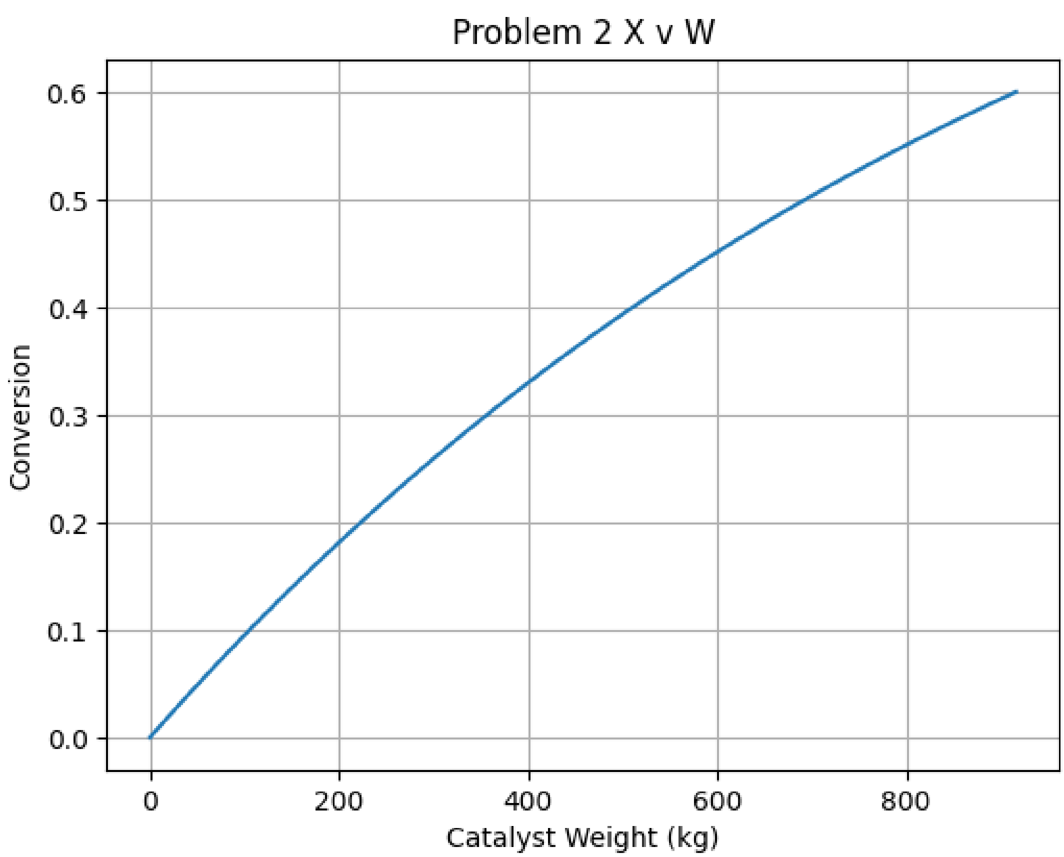
```
ode_args = (p2_ode, [0, W*1e3], [0])
ode_kwargs = {
    'method': "Radau",
    'atol': 1e-8,
    'rtol': 1e-8,
}

p2_sol = solve_ivp(*ode_args, **ode_kwargs)

print(f"Final X: {p2_sol.y[0][-1]}")

plot(p2_sol.t/1000, p2_sol.y[0])
xlabel("Catalyst Weight (kg)")
ylabel("Conversion")
title("Problem 2 X v W")
grid()
```

```
Final X: 0.6000021918225731
```



k_c is 400,000 times larger than k', and so the reaction is external mass transfer limited because the internal diffusion is very fast.

$k_c \propto \frac{d_p^{1/2}}{dp} \propto d_p^{-1/2}$

As the partical diameter increases, k_c becomes smaller.

3 Problem 3

3.1 Part A

See end for plot.

3.2 Part B

See end for plot.

$\eta = \frac{1.2}{1.8} = \boxed{0.67}$

3.3 Part C

See end for plot.

$\Omega = \frac{0.2}{0.6} = \boxed{0.33}$

4 Problem 4

4.1 Part A

$D_A \frac{d^2 C_A}{dz^2} = k$

$\psi = \frac{C_A}{C_{As}}$, $\lambda = \frac{z}{L}$

$C_A = \psi C_{AS}$, $z = \lambda L$

$D_A \frac{d^2(\psi C_{AS})}{d(\lambda L)^2} = k$

$D_A \frac{C_{AS}}{L^2} \frac{d^2\psi}{d\lambda^2} = k$

$\frac{d^2\psi}{d\lambda^2} = \frac{kL^2}{D_A C_{AS}}$

$\frac{d\psi}{d\lambda} = 0$ at $\lambda = 0$

$\frac{d\psi}{d\lambda} = \frac{kL^2}{D_A C_{AS}} \lambda$

$\psi = \frac{kL^2}{2D_A C_{AS}} \lambda^2 + C$

$\psi = 1$ at $\lambda = 1$

$C = 1 - \frac{kL^2}{2D_A C_{AS}}$

$\psi = 1 + \frac{kL^2}{2D_A C_{AS}} \left(\lambda^2 - 1\right)$

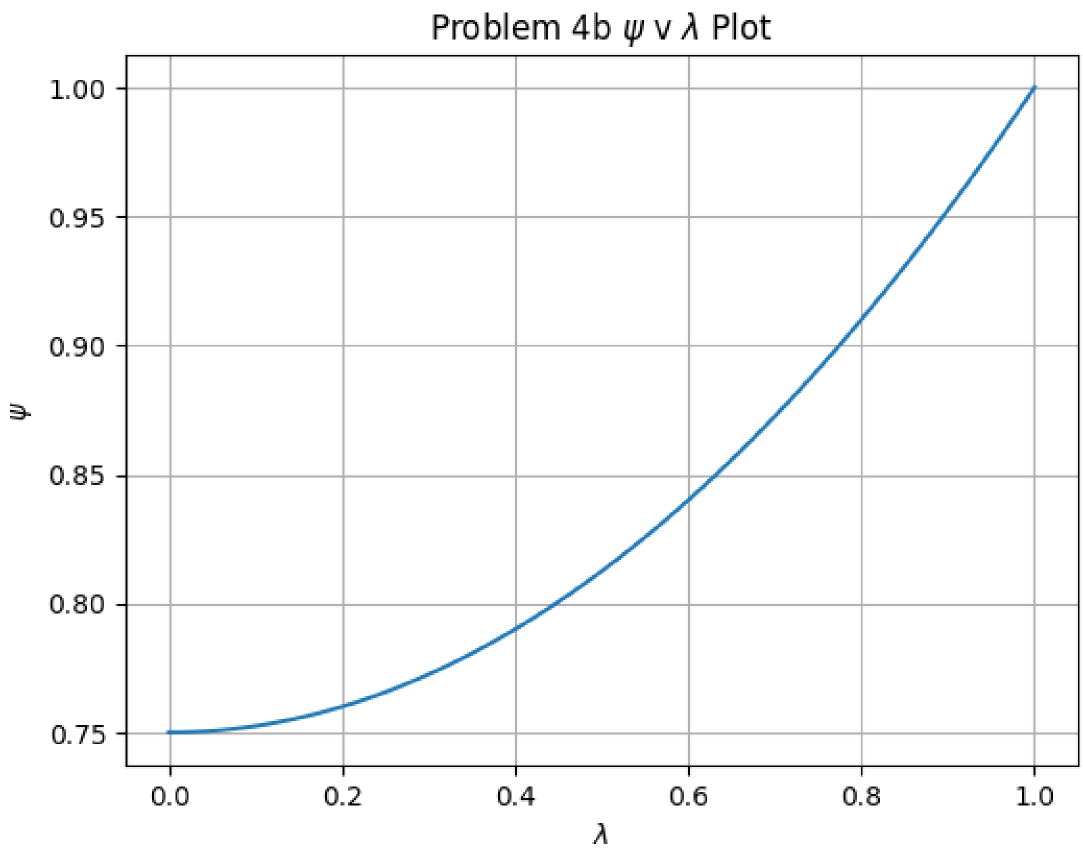
$\phi_0^2 = \frac{kL^2}{2D_A C_{AS}}$

$\psi = 1 + \phi_0^2 \left(\lambda^2 - 1\right)$

4.2 Part B

[ ]:
```
lamba = linspace(0, 1, 100)
phi = 0.5
psi = lambda lamba: 1 + phi**2 * (lamba**2 - 1)

plot(lamba, psi(lamba))
xlabel(r"$\lambda$")
ylabel(r"$\psi$")
title(r"Problem 4b $\psi$ v $\lambda$ Plot")
grid()
```



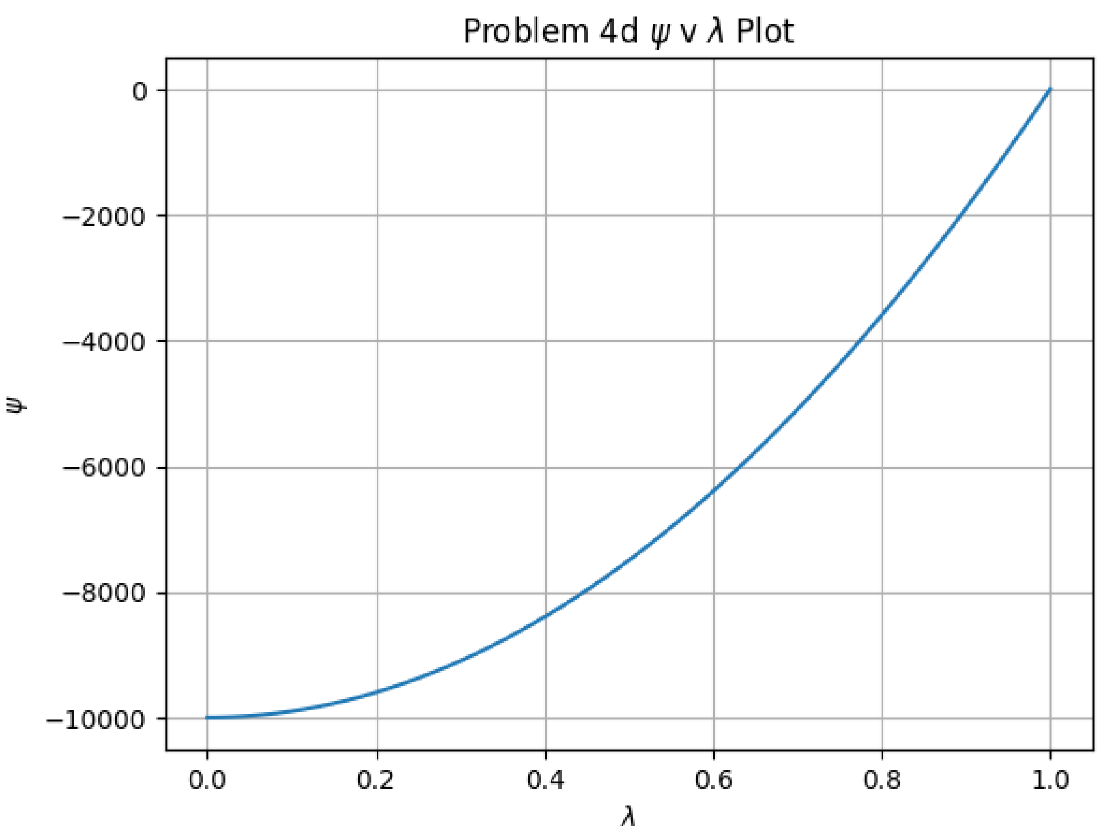
4.3 Part C

η will be 1 for small values of the Thiele modulus because the reaction becomes external diffusion limited.

4.4 Part D

```
[ ]: lamba = linspace(0, 1, 100)
phi = 100
psi = lambda lamba: 1 + phi**2 * (lamba**2 - 1)

plot(lamba, psi(lamba))
xlabel(r"$\lambda$")
ylabel(r"$\psi$")
title(r"Problem 4d $\psi$ v $\lambda$ Plot")
grid()
```



ψ became negative for a large Thiele modulus. It is not possible to have negative concentration values.