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## CH EN 3553

### Homework 5

#### Problem 1

##### Part a

Differential Equation for  $c_A$

$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt}$$

$$F_{A0} = c_{A0} \cdot \dot{V}_0,$$

$$F_A = c_A \cdot \dot{V},$$

$$N_A = c_A \cdot V,$$

$$r_A = -k_1 c_A^2 \Rightarrow$$

$$c_{A0} \cdot \dot{V}_0 - c_A \cdot \dot{V} + \int_0^V -k_1 c_A^2 dV = \frac{d[c_A \cdot V]}{dt}.$$

Assuming the tank is perfectly mixed, the concentration of A doesn't change with location in the tank  $\Rightarrow$

$$c_{A0} \cdot \dot{V}_0 - c_A \cdot \dot{V} - k_1 c_A^2 V = \frac{d[c_A \cdot V]}{dt}.$$

Knowing that the outlet volumetric flowrate is 1.5 times the inlet flowrate  $\Rightarrow$

$$\dot{V} = 1.5 \dot{V}_0 \Rightarrow$$

$$c_{A0} \cdot \dot{V}_0 - c_A \cdot 1.5 \dot{V}_0 - k_1 c_A^2 V = \frac{d[c_A \cdot V]}{dt}.$$

Distributing the derivative on the right hand side  $\Rightarrow$

$$c_{A0} \cdot \dot{V}_0 - c_A \cdot 1.5 \dot{V}_0 - k_1 c_A^2 V = c_A \frac{dV}{dt} + V \frac{dc_A}{dt}.$$

Knowing that

$$\frac{dV}{dt} = \dot{V}_{in} - \dot{V}_{out} = \dot{V}_0 - \dot{V} \Rightarrow$$

$$c_{A0} \cdot \dot{V}_0 - c_A \cdot 1.5\dot{V}_0 - k_1 c_A^2 V = c_A(\dot{V}_0 - \dot{V}) + V \frac{dc_A}{dt} = c_A(-0.5\dot{V}_0) + V \frac{dc_A}{dt}.$$

Simplifying and solving for  $\frac{dc_A}{dt}$  yields

$$\frac{dc_A}{dt} = \frac{c_{A0}\dot{V}_0 - c_A\dot{V}_0}{V} - k_1 c_A^2.$$

The volume at time  $t$  is given by

$$V = V_0 + (\dot{V}_0 - \dot{V}) \cdot t = V_0 + (\dot{V}_0 - 1.5\dot{V}_0) \cdot t = V_0 - 0.5\dot{V}_0 t \Rightarrow$$

$$\boxed{\frac{dc_A}{dt} = \frac{\dot{V}_0}{V_0 - 0.5\dot{V}_0 t} (c_{A0} - c_A) - k_1 c_A^2}$$

### Differential Equation for $c_P$

Using the equation

$$r_{total} = \frac{r_A}{v_A} \Rightarrow$$

$$r_{total} = \frac{-k_1 c_A^2}{-1} = k_1 c_A^2.$$

Using the same relationship will yield the equation for  $r_P$ .

$$r_{total} = \frac{r_P}{v_P} \Rightarrow r_P = v_P r_{total} \Rightarrow r_P = 2k_1 c_A^2.$$

$$F_{P0} - F_P + \int_0^V r_P dV = \frac{dN_P}{dt}$$

$$F_{P0} = 0,$$

$$F_P = c_P \dot{V},$$

$$r_P = 2k_1 c_A^2,$$

$$N_P = c_P \cdot V \Rightarrow$$

$$-c_P \dot{V} + \int_0^V 2k_1 c_A^2 = \frac{d[c_P \cdot V]}{dt}.$$

Assuming the tank is perfectly mixed, the concentration of P doesn't change with location in the tank  $\Rightarrow$

$$-c_P \dot{V} + 2k_1 c_A^2 V = \frac{d[c_P \cdot V]}{dt}.$$

Knowing that the outlet volumetric flowrate is 1.5 times the inlet flowrate  $\Rightarrow$

$$\dot{V} = 1.5 \dot{V}_0 \Rightarrow$$

$$-1.5c_P \dot{V}_0 + 2k_1 c_A^2 V = \frac{d[c_P \cdot V]}{dt}.$$

Distributing the derivative on the right hand side  $\Rightarrow$

$$-1.5c_P \dot{V}_0 + 2k_1 c_A^2 V = c_P \frac{dV}{dt} + V \frac{dc_P}{dt}.$$

The relationship of  $\frac{dV}{dt}$  to  $\dot{V}_0$  is

$$\frac{dV}{dt} = \dot{V}_{in} - \dot{V}_{out} = \dot{V}_0 - \dot{V} = \dot{V}_0 - 1.5\dot{V}_0 = -0.5\dot{V}_0 \Rightarrow$$

$$-1.5c_P \dot{V}_0 + 2k_1 c_A^2 V = c_P(-0.5\dot{V}_0) + V \frac{dc_P}{dt}.$$

Simplifying and solving for  $\frac{dc_P}{dt}$  yields

$$\frac{dc_P}{dt} = \frac{-c_P \dot{V}_0}{V} + 2k_1 c_A^2.$$

The volume at time  $t$  is given by

$$V = V_0 + (\dot{V}_0 - \dot{V}) \cdot t = V_0 + (\dot{V}_0 - 1.5\dot{V}_0) \cdot t = V_0 - 0.5\dot{V}_0 t \Rightarrow$$

$$\boxed{\frac{dc_P}{dt} = \frac{-c_P \dot{V}_0}{V_0 - 0.5\dot{V}_0 t} + 2k_1 c_A^2}.$$

## Part b

```
In [1]: import numpy as np
        from scipy.integrate import odeint
```

```
In [2]: #constants and known values
k_1=0.02 #L/(mol*s)
k_1_hours=k_1*3600 #L/(mol*hr)
t=2 #hr
V_0=10 #L/hr
V_0=1000 #L
n_A0=200 #mol
c_A0=n_A0/V_0 #mol/L
```

```
In [3]: #creating coupled ODE to integrate
def func(v,t):
    c_A,c_P=v
    dvdt=[(V_0/(V_0-0.5*V_0*t))*(c_A0-c_A)-k_1_hours*c_A**2,(-c_P*V_0)/(
V_0-0.5*V_0*t)+2*k_1_hours*c_A**2]
    return dvdt

#initial conditions
v0=[c_A0,0]

#time array
t=np.linspace(0,2,10000) #hours

#solution array
sol=odeint(func,v0,t)

#array of just c_P
c_P=sol[:,1]

#integrating c_P with respect to t
integral=sum(c_P)*t[-1]/len(t) #(mol*hr)/L

N_P=integral*1.5*V_0 #mol
print(N_P)

#NP=np.trapz(c_P*V_0)
#print(NP)
```

10.547139690563396

10.547moles of product leaves the reactor.

## Problem 2

part a

$$F_A \Big|_z - F_A \Big|_{z+\Delta z} = F_{A,leak} \Big|_z \Rightarrow$$

$$F_{A,leak} \Big|_z = c_A \Big|_z \left( \dot{V}_A \Big|_z - \dot{V}_A \Big|_{z+\Delta z} \right).$$

$$\frac{d\dot{V}_A}{dz} = \frac{\dot{V}_A \Big|_{z+\Delta z} - \dot{V}_A \Big|_z}{\Delta z} \Rightarrow$$

$$\left( \dot{V}_A \Big|_z - \dot{V}_A \Big|_{z+\Delta z} \right) = -\Delta z \frac{d\dot{V}_A}{dz} \Rightarrow$$

$$\boxed{F_{A,leak} \Big|_z = - \left( c_A \Big|_z \right) \frac{d\dot{V}_A}{dz} \Delta z}$$

**part b**

$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt}$$

$$r_A = -kc_A$$

Assuming the concentration doesn't change in the radially

$$\int_0^V r_A dV = r_A V = -kc_A A_c \Delta z \Rightarrow$$

$$\boxed{F_A \Big|_z - F_A \Big|_{z+\Delta z} + \left( c_A \Big|_z \right) \frac{d\dot{V}_A}{dz} \Delta z - k \left( c_A \Big|_z \right) A_c \Delta z = 0}$$

**part c**

$$F_A \Big|_z - F_A \Big|_{z+\Delta z} + \left( c_A \Big|_z \right) \frac{d\dot{V}_A}{dz} \Delta z - k \left( c_A \Big|_z \right) A_c \Delta z = 0 \Rightarrow$$

$$F_A \Big|_z - F_A \Big|_{z+\Delta z} + \left( c_A \Big|_z \right) \frac{d\dot{V}_A}{dz} \Delta z = k \left( c_A \Big|_z \right) A_c \Delta z \Rightarrow$$

$$\frac{F_A \Big|_z - F_A \Big|_{z+\Delta z}}{\Delta z} + \left( c_A \Big|_z \right) \frac{d\dot{V}_A}{dz} = k \left( c_A \Big|_z \right) A_c$$

Taking  $\lim_{\Delta z \rightarrow 0} \Rightarrow$

$$\frac{-dF_A}{dz} + c_A \Big|_z \frac{d\dot{V}_A}{dz} = k c_A \Big|_z A_c$$

Plugging in

$$F_A = F_{A0}(1 - X_A) \Rightarrow$$

$$\frac{-d[F_{A0}(1-X_A)]}{dz} = F_{A0} \frac{dX_A}{dz} \Rightarrow$$

$$\boxed{F_{A0} \frac{dX_A}{dz} + c_A \Big|_z \frac{d\dot{V}_A}{dz} = k c_A \Big|_z A_c}$$

**part d**

$$\frac{dX_A}{dz} = \frac{k c_A \Big|_z A_c - c_A \Big|_z \frac{d\dot{V}_A}{dz}}{F_{A0}} = \frac{c_A \Big|_z}{F_{A0}} \left( k A_c - \frac{d\dot{V}}{dz} \right)$$

$$\frac{d\dot{V}}{dz} = \dot{V}_0 \left( 0 - \frac{1}{L} \right) = \frac{-\dot{V}_0}{L} \Rightarrow$$

$$\frac{dX_A}{dz} = \frac{c_A \Big|_z}{F_{A0}} \left( k A_c + \frac{\dot{V}_0}{L} \right)$$

$$c_A \Big|_z = \frac{F_A}{\dot{V} \Big|_z} = \frac{F_{A0}(1-X_A)}{\dot{V}_0(1-\frac{z}{L})} \Rightarrow$$

$$\boxed{\frac{dX_A}{dz} = \frac{1-X_A}{1-\frac{z}{L}} \left( \frac{k A_c}{\dot{V}_0} + \frac{1}{L} \right)}$$

**part e**

$$\frac{dX_A}{dz} = \frac{1-X_A}{1-\frac{z}{L}} \left( \frac{kA_c}{\dot{V}_0} + \frac{1}{L} \right)$$

$$\frac{dX_A}{1-X_A} = \frac{1}{1-\frac{z}{L}} \left( \frac{kA_c}{\dot{V}_0} + \frac{1}{L} \right) dz$$

$$\int \frac{dX_A}{1-X_A} = \left( \frac{kA_c}{\dot{V}_0} + \frac{1}{L} \right) \int \frac{dz}{1-\frac{z}{L}}$$

$$-\ln(1-X_A) = \left( \frac{kA_c}{\dot{V}_0} + \frac{1}{L} \right) \int \frac{dz}{1-\frac{z}{L}}$$

$$\text{let } u = 1 - \frac{z}{L}$$

$$\frac{du}{dz} = \frac{-1}{L} \Rightarrow dz = -L du \Rightarrow$$

$$\int \frac{dz}{1-\frac{z}{L}} = -L \int \frac{du}{u} = -L \ln(u) = -L \ln\left(1 - \frac{z}{L}\right) \Rightarrow$$

$$-\ln(1-X_A) = \left( \frac{kA_c}{\dot{V}_0} + \frac{1}{L} \right) (-L \ln(1 - \frac{z}{L}))$$

$$\ln(1-X_A) = \left( \frac{LkA_c}{\dot{V}_0} + 1 \right) \ln(1 - \frac{z}{L})$$

$$\ln(1-X_A) = \ln(1 - \frac{z}{L}) \text{exponent} \left( \frac{LkA_c}{\dot{V}_0} + 1 \right)$$

$$1-X_A = \left(1 - \frac{z}{L}\right) \text{exponent} \left( \frac{LkA_c}{\dot{V}_0} + 1 \right)$$

$$\boxed{X_A = 1 - \left(1 - \frac{z}{L}\right) \text{exponent} \left( \frac{LkA_c}{\dot{V}_0} + 1 \right)}$$

### Problem 3

in - out + generation - diffusion = accumulation

$$F_i \Big|_V - F_i \Big|_{V+\Delta V} + r_i \Delta V - R_i \Delta V = \frac{dF_i}{dt}$$

Because this is a differential volume element

$$\frac{dF_i}{dt} = 0 \Rightarrow$$

$$F_i \Big|_V - F_i \Big|_{V+\Delta V} + r_i \Delta V - R_i \Delta V = 0$$

Dividing both sides by  $\Delta V \Rightarrow$

$$\frac{F_i \Big|_V - F_i \Big|_{V+\Delta V}}{\Delta V} + r_i - R_i = 0$$

$$\frac{F_i \Big|_{V+\Delta V} - F_i \Big|_V}{\Delta V} = \frac{dF_i}{dV} \Rightarrow$$

$$\frac{dF_i}{dV} = r_i - R_i$$

$$\frac{dF_i}{dV} = \frac{dF_i}{A_c z} \Rightarrow$$

$$\frac{dF_i}{dz} = A_c(r_i - R_i) \Rightarrow$$

$$\frac{dF_A}{dz} = A_c(r_A - R_A)$$

$$\frac{dF_B}{dz} = A_c(r_B - R_B)$$

$$\frac{dF_C}{dz} = A_c r_C$$

$$r_A = -k_1 c_A + k_{-1} c_B c_C^2$$

$$K_C = \frac{k_1}{k_{-1}} \Rightarrow k_{-1} = \frac{k_1}{K_C} \Rightarrow$$

$$r_A = -k_1 c_A + \frac{k_1}{K_C} c_B c_C^2$$



Because this is an isothermal, isobaric reactor

$$c_i = \frac{c_T F_i}{F_T} \Rightarrow$$

$$r_A = -k_1 \frac{c_T F_A}{F_T} + \frac{k_1}{K_C} \frac{c_T F_B}{F_T} \left( \frac{c_T F_C}{F_T} \right)^2 \Rightarrow$$

$$r_A = k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right)$$

$$\frac{r_A}{v_A} = \frac{r_B}{v_B} = \frac{r_C}{v_C} \Rightarrow$$

$$r_B = -r_A = -k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right)$$

$$r_C = -2r_A = -2k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right)$$

$$R_i = \beta_i c_i = \frac{\beta_i c_T F_i}{F_T} \Rightarrow$$

$$\frac{dF_A}{dz} = A_c \left[ k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right) - \frac{\beta_A c_T F_A}{F_T} \right]$$

$$\frac{dF_B}{dz} = A_c \left[ -k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right) - \frac{\beta_B c_T F_B}{F_T} \right]$$

$$\frac{dF_C}{dz} = A_c \left[ -2k_1 \left( \frac{-c_T F_A}{F_T} + \frac{c_T^3 F_B F_C^2}{F_T^3 K_C} \right) \right]$$

$$F_T = F_A + F_B + F_C \Rightarrow$$

$$\frac{dF_A}{dz} = A_c \left[ k_1 \left( \frac{-c_T F_A}{F_A + F_B + F_C} + \frac{c_T^3 F_B F_C^2}{(F_A + F_B + F_C)^3 K_C} \right) - \frac{\beta_A c_T F_A}{F_A + F_B + F_C} \right]$$

$$\frac{dF_B}{dz} = A_c \left[ -k_1 \left( \frac{-c_T F_A}{F_A + F_B + F_C} + \frac{c_T^3 F_B F_C^2}{(F_A + F_B + F_C)^3 K_C} \right) - \frac{\beta_B c_T F_B}{F_A + F_B + F_C} \right]$$

$$\frac{dF_C}{dz} = A_c \left[ -2k_1 \left( \frac{-c_T F_A}{F_A + F_B + F_C} + \frac{c_T^3 F_B F_C^2}{(F_A + F_B + F_C)^3 K_C} \right) \right]$$

```
In [4]: from matplotlib import pyplot as plt
```

```
In [5]: #constants
k1=10 #1/min
Kc=0.01 #mol^2/L^2
Ba=1 #1/min
Bb=40 #1/min
F_A0=100 #mol/min
V_0=100 #L/min
Ac=2 #dm^2
L=10 #dm
c_T=F_A0/V_0 #mol/L
```

```
In [6]: #creating coupled ODE to integrate
def func(v,z):
    F_A=v[0]
    F_B=v[1]
    F_C=v[2]
    dF_Adt=Ac*(k1*(-c_T*F_A/(F_A+F_B+F_C)+(c_T**3)*F_B*(F_C**2)/((F_A+F_
B+F_C)**3*Kc))-Ba*c_T*F_A/(F_A+F_B+F_C))
    dF_Bdt=Ac*(-k1*(-c_T*F_A/(F_A+F_B+F_C)+(c_T**3)*F_B*(F_C**2)/((F_A+F
_B+F_C)**3*Kc))-Bb*c_T*F_B/(F_A+F_B+F_C))
    dF_Cdt=-2*Ac*k1*(-c_T*F_A/(F_A+F_B+F_C)+(c_T**3)*F_B*(F_C**2)/((F_A+
F_B+F_C)**3*Kc))
    dvdt=[dF_Adt,dF_Bdt,dF_Cdt]
    return dvdt
```

```

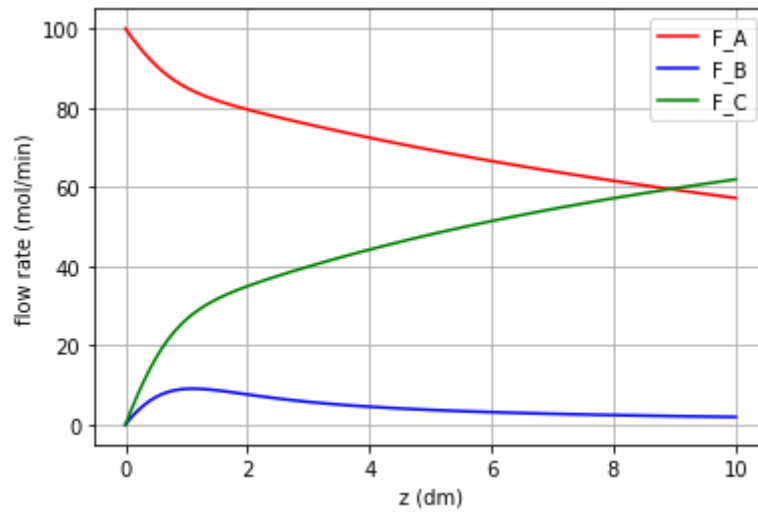
In [7]: #initial conditions
v0=[100,0,0]

#distance array
z=np.linspace(0,L,100) #dm

#solution array
sol=odeint(func,v0,z)

#graphing
plt.plot(z,sol[:,0], 'r-', label='F_A')
plt.plot(z,sol[:,1], 'b-', label='F_B')
plt.plot(z,sol[:,2], 'g-', label='F_C')
plt.xlabel('z (dm)')
plt.ylabel('flow rate (mol/min)')
plt.legend(loc='best')
plt.grid()
plt.show()

```



## Problem 4

### part a

$$F_{NO_2,0} - F_{NO_2} + \int_0^V r_{NO_2} dV = \frac{dN_{NO_2}}{dt}$$

$$F_{NO_2,0} - F_{NO_2} + r_{NO_2} V = 0$$

$$r_{NO_2} = \frac{F_{NO_2} - F_{NO_2,0}}{V}$$

$$F_{NO_2} = F_{NO_2,0}(1 - X_{NO_2}) \Rightarrow$$

$$r_{NO_2} = \frac{F_{NO_2,0}(1 - X_{NO_2}) - F_{NO_2,0}}{V} = \frac{-F_{NO_2,0} X_{NO_2}}{V} \Rightarrow$$

$$\boxed{-r_{NO_2} = \frac{F_{NO_2,0} X_{NO_2}}{V}}$$

The equation is algebraic (instead of differential) because the differential reactor operates at very low conversions, so the reactant concentration is essentially constant throughout the reactor.

### part b

$$-r_{NO_2} = kc_{NO_2}^n = \frac{F_{NO_2,0} X_{NO_2}}{V}$$

$$X_{NO_2} = \frac{V}{F_{NO_2,0}} kc_{NO_2}^n$$

graphing  $X_{NO_2}$  vs  $\frac{V}{F_{NO_2,0}}$  makes the slope =  $kc_{NO_2}^n$

If three different initial concentrations show up on the same linear line, this shows that the slope is independent of the initial concentration, so  $n = 0$ .

$$\boxed{order = 0}$$

## part c

Estimating the activation energy should make us think of the arranius equation

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = \frac{-E_a}{RT} + \ln(A)$$

$$k = \frac{X_{NO_2}}{V/F_{NO_2,0}}$$

By plotting  $\ln(k)$  vs  $\frac{1}{T}$ , the slope will equal  $\frac{-E_a}{R}$ .

Two data points are chosen that must be on different temperature lines. For my solution, I chose the triangle on the T=300 line near the middle of the line as my first data point. My second data point was the circle on the far right end of the T=200 line. I estimated the position of these data points, then used the method described above to estimate  $E_a$ .

```
In [8]: import numpy as np

X=np.array([0.51,0.50]) #conversion (X)
VoverF_NO2=np.array([0.75*10**5,3.8*10**5]) #V/F_NO2 (m3*h)/(mol)
T=np.array([300+273.15,200+273.15]) #K
k=X/VoverF_NO2 #mol/(m3*h)
R=.008314 #kJ/(mol*K)
y=np.log(k) #mol/(m3*h)
x=T**(-1) #1/K
slope=(y[1]-y[0])/(x[1]-x[0]) #(mol*K)/(m3*h)
Ea=-R*slope #J/(mol*K) * (mol*K)/(m3*h) = J/(m3*h)
Ea_rounded=round(Ea,2)
print (Ea_rounded,'kJ/(mol*K)')

37.03 kJ/(mol*K)
```

The estimated activation energy is

$$E_a = 37.03 \frac{kJ}{mol \cdot K}.$$