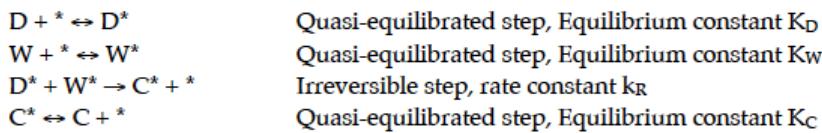


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**CH EN 3553**

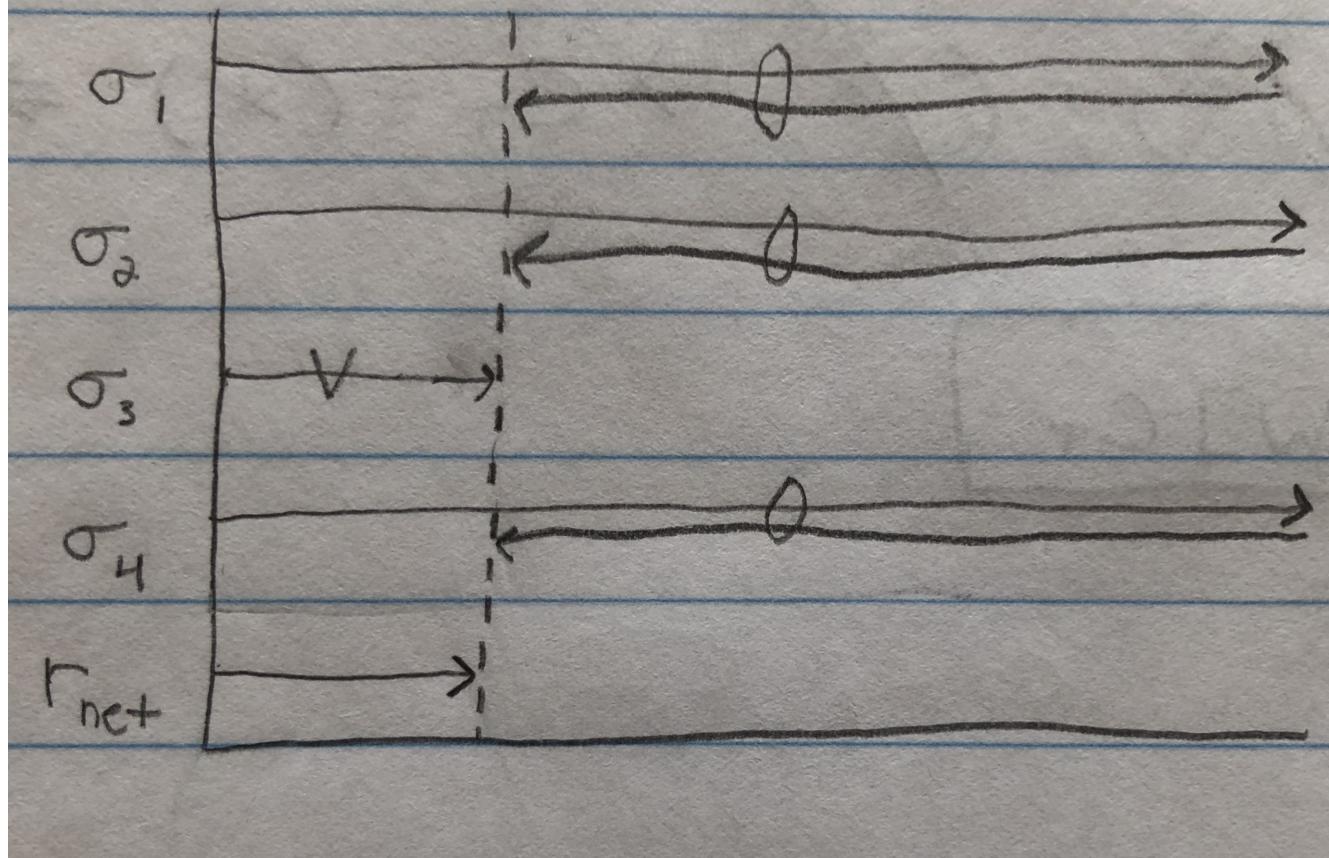
**Homework 10**

MN Chemicals, always on the cutting edge of catalysis and reactor engineering, has developed a new catalyst for converting dirt (D) to cash (C). When dirt is in the presence of the new catalyst along with water (W), it converts to cash. Note that the cost of the catalyst is much less than that cash produced from it. This catalyst has a total number of sites  $C_T$ . The heterogeneously catalyzed mechanism is shown below. \* represents open binding sites on the catalyst surface. Assume that the stoichiometric numbers for each step are 1.



- a. Draw an arrow diagram for this reaction system showing the relative rates of each step in the mechanism.
- b. What is the overall rate of the reaction expressed in terms of quantities that are easily measured and the equilibrium and rate constants?
- c. If \* is MASI, what is the overall rate of the reaction?
- d. Given that at 20% of the way into the catalyst particle from the surface, the concentration of D is 1/10 of the value at the surface, what is the internal effectiveness factor for this system? Assume that the reaction is first order in D and zero order in W. [0.2]

**part a solution**



**part b solution**

$$b) r_{net} = r_3 = k_r(D^*)(W^*)/c_T$$

$$K_D = \frac{(D^*)}{(D)(*)} \Rightarrow (D^*) = K_D(D)(*)$$

$$K_w = \frac{(W^*)}{(W)(*)} \Rightarrow (W^*) = K_w(W)(*) \Rightarrow$$

$$r_{net} = k_r K_D K_w (D)(W)(*)^2 / c_T$$

$$C_T = (*) + (D^*) + (W^*) + (C^*)$$

$$K_C = \frac{(C)(*)}{(C^*)} \Rightarrow (C^*) = \frac{(C)(*)}{K_C} \Rightarrow$$

$$C_T = (*) + K_D(D)(*) + K_w(W)(*) + \frac{(C)(*)}{K_C} \Rightarrow$$

$$(*) = \frac{C_T}{1 + K_D(D) + K_w(W) + \frac{(C)}{K_C}} \Rightarrow$$

$$\boxed{r_{net} = \frac{k_r K_D K_w [D][W] C_T}{(1 + K_D[D] + K_w[W] + \frac{[C]}{K_C})^2}}$$

**part c solution**

$$C_T = (*) + (\cancel{D}^*) + (\cancel{W}^*) + (\cancel{C}^*) \Rightarrow C_T = (*) \Rightarrow$$

$$r_{net} = k_R K_D K_W [D][W] C_T$$

## part d solution

$$\frac{C_D}{C_{DS}} = \frac{1}{\lambda} \frac{\sinh(\phi_1 \lambda)}{\sinh(\phi)}$$

```
In [3]: from scipy.optimize import fsolve
from math import sinh

def func(phi):
    C_D=.1
    C_DS=1
    λ=0.80
    r=C_D/C_DS-1/λ*sinh(φ*λ)/sinh(φ)
    return r

sol=fsolve(func,0.2)
print('φ=',sol)

φ= [12.62864321]
```

Because  $2 < \phi < 20$

$$\eta = \frac{3}{φ^2} (φ - 1)$$

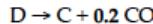
```
In [4]: η=3/sol**2*(sol-1)
print('η=',η)

η= [0.21874438]
```

$$\boxed{\eta = 0.219}$$

Due to the high internal mass transfer limitations on this system, the researchers at MN Chemicals have decided that a heterogeneous system was not the best path forward for

this system. They decided to work on a new reaction system to convert dirt to cash. At moderate pressure (10 atm) and a significant amount of heat, they can gasify the dirt to form cash. The reaction proceeds as a first order reaction in D. Water is not necessary for this reaction. However a side product, carbon monoxide (CO) is also produced. The reaction is listed below.



Assume that all substances are ideal gases.

- e. When a PFR reactor with a jacketed heat exchanger is run under isothermal and isobaric conditions at 700K, what reactor volume is needed to achieve a conversion of 60%? Assume that the first order rate constant at 700K is 0.1/s and that the activation energy for the reaction is 5000 J/mol. The feed is pure gasified dirt. The specific heat capacities of all substances is 35 J/(mol\*K), which is constant over all temperatures. The volumetric flow rate at 700K is 5 L/s. [50 L]
- f. Qualitatively, how does this conversion compare with that calculated by the segregation model?
- g. What is the highest conversion possible if the reaction is assumed to be reversible? The equilibrium constant is 8 (mol/L)<sup>0.2</sup> at 700K. [0.95]
- h. If the heat of reaction is -5000 J/mol for all temperatures, what is the maximum heat load on the heat exchanger? [2.5 kW]
- i. There is a problem with the heat exchanger which causes it to completely fail. The reactor is very well insulated. What is the temperature and conversion at the outlet of the reactor? [X = 0.6, T = 775K] Use the same volume as calculated in part e and assume that the reaction is irreversible again. What would the volume of the reactor have to be operating in adiabatic mode to reach 75% conversion? [75 L]
- j. Assume that the heat exchanger has been fixed now by star plumbers Mario and Luigi. However it is understood that the cash will undergo a phase transition from gas directly to solid when its mole fraction in the gas phase is 0.2. What is the conversion when the cash begins to deposit? [0.21]

## part e solution

$$\text{e) } V_{PFR} = F_D \int_0^X \frac{dx}{-r_D} \quad -r_D = k C_D \Rightarrow$$

$$V_{PFR} = C_D \dot{V} \int_0^X \frac{dx}{k C_D} ; PV = nRT \Rightarrow \frac{P}{V} = \frac{n}{RT} = C_D ; C_D = \frac{C_{D0}(1-X)}{1+0.2X}$$

$$\dot{V} = \frac{\dot{V}}{k} \int_0^X \frac{dx}{\frac{1-X}{1+0.2X}} = \frac{\dot{V}}{k} \int \frac{1+0.2X}{1-X} dx =$$

```
In [6]: import numpy as np
from scipy.integrate import trapz

v=5 #L/s
k=0.1 #1/s
x=np.linspace(0,0.60,1000)

y=(1+0.2*x)/(1-x)

v=v/k*trapz(y,x)
print('v=',v)

v= 48.977453381375206
```

$$V_{PFR} = 48.98L$$

## part f solution

The segregation model depends on concentration. Because the concentration of dirt doesn't appear in the equation for the volume of the PFR (derived above), the volume of the PFR calculated with the segregation model will be the same as the volume calculated for an ideal PFR.

## part g solution

$$g) \frac{(C)(C_0)^{0.2}}{(D)} = K$$

$$(D) = \frac{C_{D0}(1-X)}{1+0.2X} \quad (C) = \frac{C_{D0}(1-\frac{V_c}{V_D}X)}{1+0.2X} = \frac{C_{D0}X}{1+0.2X}$$

$$(C_0) = \frac{C_{D0}(1-\frac{0.2}{1+0.2}X)}{1+0.2X} = \frac{0.2C_{D0}X}{1+0.2X} \Rightarrow$$

$$K = \left( \frac{C_{D0}X}{1+0.2X} \right) \left( \frac{0.2C_{D0}X}{1+0.2X} \right)^{0.2} = \left( \frac{X}{1+X} \right) \left( \frac{0.2C_{D0}X}{1+0.2X} \right)^{0.2} = K$$

```
In [7]: P=10 #atm
R=0.08205 #L*atm/(mol*K)
T=700 #K
C_D0=P/(R*T) #mol/L
K=8 #(mol/L)^0.2

def fun(X):
    r=K-(X/(1-X))*(0.2*C_D0*X/(1+0.2*X))**0.2
    return r

solution=fsover(fun,0.95)
print('X=',solution)

X= [0.94253081]
```

The highest conversion possible is  $X = 0.943$ .

## part h solution

$$\frac{dE^{\circ}}{dx} = \dot{Q} - \dot{W}_s - F_{D0} \sum_i C_{P,i} (T_f^{\circ} - T_o) - F_{D0} X (\Delta H_{rxn}^{\circ}(T_R) + \Delta \dot{Q}_p(T - T_R))$$

$$\dot{Q} = \dot{Q} - F_{D0} X \Delta H_{rxn} \Rightarrow \dot{Q} = F_{D0} X \Delta H_{rxn} = C_{D0} V \times \Delta H_{rxn}$$

```
In [8]: x=0.60
ΔH=-5000 #J/mol

Q=C_D0*V*x*ΔH
print('Q=', Q, 'W')
```

$$Q = -2611.6479498563594 \text{ W}$$

The heat exchanger must be able to remove  $2612 \text{ W}$ .

### part i solution

$$\frac{dE^{\circ}}{dT} = \dot{Q} - \dot{W}_S - F_{D0} \sum \Theta_i c_{pi} (T - T_0) - F_{D0} X (\Delta H_{rxn}^{\circ}(T_R) + \Delta \hat{C}_p (T - T_R))$$

$$0 = \sum \Theta_i c_{pi} (T - T_0) + X (\Delta H_{rxn}^{\circ} + \Delta \hat{C}_p (T - T_R))$$

$$\Delta C_p = \sum \frac{V_i}{F_{D0}} C_{pi} = \frac{-1}{-1} (35) + \frac{1}{-1} (35) + \frac{0.2}{-1} (35) = -7 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\sum \Theta_i c_{pi} = C_p \sum \Theta_i = (35) \left( \frac{0}{F_{D0}} + \frac{0}{F_{D0}} + \frac{F_{D0}}{F_{D0}} \right) = 35 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$-\sum \Theta_i c_{pi} (T - T_0) = X \Delta H_{rxn}^{\circ}(T_R) + X \Delta \hat{C}_p (T - T_R) \Rightarrow$$

$$\sum \Theta_i c_{pi} (T + T_0) + X \Delta \hat{C}_p (T + T_R) = X \Delta H_{rxn}^{\circ}(T_R) \Rightarrow$$

$$\sum \Theta_i c_{pi} T + \sum \Theta_i c_{pi} T_0 + X \Delta \hat{C}_p T + X \Delta \hat{C}_p T_R = X \Delta H_{rxn}^{\circ}(T_R) \Rightarrow$$

$$T = \frac{X \Delta H_{rxn}^{\circ}(T_R) + X \Delta \hat{C}_p T_R + \sum \Theta_i c_{pi} T_0}{\sum \Theta_i c_{pi} + X \Delta \hat{C}_p} \quad \leftarrow \text{energy balance}$$

$$\text{mass balance: } (D) = \frac{C_{D0} (1-X) T_0}{T (1+0.2X)}$$

$$\frac{dX}{dV} = \frac{k C_D}{F_{D0}} = \frac{k T_0 (1-X)}{V T (1+0.2X)}$$

$$k = k_{T_R} \exp \left( \frac{E_a}{R} \left( \frac{1}{T_R} - \frac{1}{T} \right) \right)$$

```
In [9]: from scipy.integrate import odeint

ΔCp=-7 #J/(mol*K)
ΣΘCp=35 #J/(mol*K)
T0=700 #K
Tr=700 #K
Ea=5000 #J/mol
V=5 #L/s
k700=0.1 #1/s
R=8.314 #J/(mol*K)
#V=48.98 #L
Cp=35 #J/(mol*K)
F_D0=V*C_D0 #mol/s

#creating differential function to integreate over

def func(X,V):
    T=(-X*ΔH+X*0.2*Cp*Tr+Cp*T0)/(Cp+X*0.2*Cp) #K
    k=k700*np.exp(Ea/R*(1/Tr-1/T)) #1/s
    dXdV=(k*C_D0*T0*(1-X))/(F_D0*T*(1+0.2*X)) #1/L
    return dXdV

#initial condition for X
initial=0 #unitless

#Volume array
V=np.linspace(0,V,100) #L

#solution array for conversion
X=odeint(func,initial,V) #unitless
print('Outlet conversion =',X[-1],'.')
X=X[-1]

#plugging X back into equation for T to find final T
T=(-X*ΔH+X*0.2*Cp*Tr+Cp*T0)/(Cp+X*0.2*Cp)
print('Outlet temperature =',T,'K.')

Outlet conversion = [0.596191] .
Outlet temperature = [776.09652908] K.
```

The temperature and conversion at the outlet of the reactor are  $T = 776.1 \text{ K}$  and  $X = 0.596$  respectively.

```
In [10]: def func(V,X):
    T=(-X*ΔH+X*0.2*Cp*Tr+Cp*T0)/(Cp+X*0.2*Cp) #K
    k=k700*np.exp(Ea/R*(1/Tr-1/T)) #1/s
    dVdX=(F_D0*T*(1+0.2*X))/(k*C_D0*T0*(1-X)) #1/L
    return dVdX

#initial condition for V
initial=[0] #L

#Volume array
X=np.linspace(0,0.75,1000) #L

#solution array for conversion
V=odeint(func,initial,X) #unitless
print('Volume =',V[-1],'.')
Volume = [76.80600621] .
```

To reach 75% conversion when operating in adiabatic mode, the volume required is  $V = 76.81 \text{ L}$ .

## part j solution

$$Y_C = 0.2 = \frac{F_C}{F_C + F_D + F_{CO}} ; F_C = F_{DO} X, F_D = F_{DO}(1-X),$$

$$F_{CO} = 0.2 F_{DO} X \Rightarrow Y_C = 0.2 = \frac{F_{DO} X}{F_{DO} X + F_{DO}(1-X) + 0.2 F_{DO} X} \Rightarrow$$

$$Y_C = 0.2 = \frac{X}{X + 1 - X + 0.2X} = \frac{X}{1 + 0.2X} = 0.2 \Rightarrow$$

$$X = 0.2 + 0.04X \Rightarrow X - 0.04X = 0.2 \Rightarrow$$

$$X = \frac{0.2}{1 - 0.04} \Rightarrow \boxed{X = 0.208}$$

In [ ]: