ChE445_HW7_Winter2020_Solution

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HW7. External mass transfer limitations.

due Monday, March 30, 2020. Weight: 2%

Reaction: $A + O_2 \rightarrow B$ (gas phase)

Kinetics: Intrinsically 1^{st} order to A and apparent 0^{th} order to O_2 (excess air and O_2)*

Catalyst: Spherical, 3 cm diameter, non-porous, 4 kg

Reactor: tubular PBR, i.d. 0.05 m, no pressure drop

Bed density and porosity: $500 kg/m^3$, 0.4

Other properties at reaction temperature: -Concentration of A in the entering feed $5E-4 mol/m^3$

-Diffusivity of A in air $2E-5 m^2/s$

-Kinematic viscosity of the fluid $5E-5 m2/s$

-Intrinsic rate constant $8 m^3(fluid)/(m3(bed)s)$

External temperature gradients are negligible at all conditions in this assignment, but there is the possibility of external MTL and we have to find conditions to maximize the production of B. The system can be assumed to be constant density because of the excess oxygen (air).

Question 1. For volumetric flow rates (reaction conditions) of 0.0005, 0.05 and $15 m^3/s$, express the surface concentration of A as a function of its bulk concentration. (hint: use k and kc). 35 pts

Question 2. Among the three cases, select the flow rate where external MTL can be ignored and calculate X_A and exit molar flow rate of product B (use ideal PBR design equation, and use bed density to have the correct units for the rate constant to be used in the mole balance for the PBR). 10 pts

Question 3. Among these three cases, select the flow rate where external MTL is severe and external diffusion is rate-limiting. Again, calculate X_A and F_B considering that the observed rate is equal to the mass transfer rate. (For bed length, use bed density, catalyst mass and the tube Ac). 15 pts

Question 4. Calculate the conversion and F_B for the third case. (Use PBR design equation with CAs but conversion is related to $C_{Ab}, not $C_{As}. Again, watch out for units of k as in **Q2**). 25 pts

Question 5. Can you explain why the conversion in the cases affected by external MTL is higher than in the case where kinetics are rate determining? If your target were to produce the highest exit F_B, which case among the three would you prefer? 10 pts

Question 6. Given that diffusivities in liquid phase are lower than those in gas phase, which reactions are more prone to mass-transfer limitations: those in gas phase or in liquid phase? 5 pts

*Note: an "apparent" order means that the reaction rate at these particular concentrations (pressures) and temperature does not depend on the oxygen pressure. The reaction may still be, for example, an intrinsic first order to oxygen:

$$-r_A = k \cdot C_A \cdot P_{O2} \tag{1}$$

But because of the excess oxygen, its partial pressure does not change significantly during the reaction, so it can be lumped into the rate constant (e.g. if there are 100 times more moles of O_2 than of A, the pressure of oxygen will drop negligibly even when all A is consumed). So, the rate law (only at these particular conditions) can be simplified to $-r_A = k* \cdot C_A$.

Answer to Q1

$$C_{As} = \frac{k_c a_c}{k + k_c a_c} C_{Ab}, \quad 1^{st}\ order \tag{2}$$

$$k_c = \frac{D_{AB} * Sh}{D_p} \tag{3}$$

$$Sh = 2 + 0.6 * Re_p^{0.5} * Sc^{1/3} \tag{4}$$

$$Sc = \frac{\nu}{D_{AB}} = \frac{5*10^{-5}}{2*10^{-5}} = 2.5 \tag{5}$$

$$Re_p = \frac{u * D_p}{\nu} = \frac{Q * D_p}{A_c * \nu} = Q * \frac{0.03}{\pi * 0.025^2 * 5 * 10^{-5}} = 305578 * Q \tag{6}$$

$$a_c = \frac{6*(1-\phi)}{D_p} = 120 \frac{m^2}{m^3_{bed}} \tag{7}$$

Check units:

$[k] = [\frac{m_l^3}{m_{bed}^3 * s}]$

$[k_c a_c] = [\frac{m}{s} * \frac{m^2}{m^3_{bed}}]$, match, ok.

$Q,\ m^3/s$	Sc	Re_p	Sh	$k_c,\ m/s$	$C_{As} = \frac{k_c*a_c}{k+k_c*a_c} * C_{Ab}$
0.0005	2.5	153	12.068	$8.04*10^{-3}$	$C_{As} = 0.11 * C_{Ab}\ \frac{mol}{m^3}$
0.05	2.5	15279	102.68	$6.84*10^{-2}$	$C_{As} = 0.51 * C_{Ab}\ \frac{mol}{m^3}$
15	2.5	4583798	1745.87	1.16	$C_{As} = 0.95 * C_{Ab}\ \frac{mol}{m^3}$

[1]:
```python
import numpy as np

nu=5*pow(10,-5)   #m2/s
DAB=2*pow(10,-5)  #m2/s
Sc=nu/DAB
Dp=0.03           #m
CA0=5*pow(10,-4) #mol/m3
rhob=500          #kg/m3
phi=0.4
k=8              #m3fl/(m3cat.s)
W=4
Id=0.05          #m
Ac=3.14*pow(Id,2)/4
ac=6*(1-phi)/Dp    #1/m

print ("Sc=",Sc)

Q=[0.0005,0.05,15]
Rep=np.zeros(len(Q))
Sh=np.zeros(len(Q))
kc=np.zeros(len(Q))
CAs_coef=np.zeros(len(Q))

for i in range(0,len(Q)):
     Rep[i]=Q[i]*Dp/(nu*Ac)
     Sh[i]=2+0.6*pow(Rep[i],1/2)*pow(Sc,1/3)
     kc[i]=Sh[i]*DAB/Dp
     CAs_coef[i]=kc[i]*ac/(k+kc[i]*ac)


print ("ac=",ac)
print ("Q=",Q)
print ("Rep=",Rep)
print ("Sh=",Sh)
print ("kc=",kc)
print ("CAs=",CAs_coef,'*CAb')
```

```
Sc= 2.5
ac= 119.99999999999999
Q= [0.0005, 0.05, 15]
Rep= [1.52866242e+02 1.52866242e+04 4.58598726e+06]
Sh= [  12.0682436   102.68243597 1745.87094535]
kc= [0.0080455  0.06845496 1.16391396]
CAs= [0.10768656 0.50661734 0.94582503] *CAb
```

Answer to Q2

When $C_{As} = \; C_{Ab}$, there are no external MTL, so at $Q = 15 \; \frac{m^3}{s}$

MB PBR:

$$F_{A0}\frac{dX}{dW} = kC_A = k\frac{F_{A0}}{Q}(1-X) \tag{8}$$

constant Q:

$$\frac{dX}{1-X} = \frac{k}{Q}dW \tag{9}$$

$$ln(\frac{1}{1-X}) = \frac{k*W}{Q} \tag{10}$$

units: from MB: $[\frac{mol}{s*kg_{cat}}] = [k*\frac{mol}{m^3_{fl}}]$

$[k] = [\frac{m^3_{fl}}{s*kg_{cat}}]$

k is given as 8 $\frac{m^3_{fl}}{m^3_{bed}*s}$ so multiply by $\frac{1}{\rho_b[kg_{cat}/m^3_{bed}]}$

$$X = 1 - exp(\frac{-k*W}{\rho_b * Q}) = 1 - exp(\frac{-8*4}{500*15}) = 0.4 \tag{11}$$

$$F_B = F_{A0} * X_A = C_{A0} * Q * X = 5*10^{-4}*15*\frac{0.4}{100} = 3*10^{-5} \;\; \frac{mol}{s} \tag{12}$$

[2]:
```python
import math
X3=1-math.exp((-k*W)/(rhob*Q[2]))
FB3=CA0*Q[2]*X3

print("X3={0:.4f}".format(X3),'%')
print ("FB3={0:.6f}".format(FB3),'mol/s')
```

```
X3=0.0043 %
FB3=0.000032 mol/s
```

Answer to Q3

When $C_{As} = 0$ ($<< C_{Ab}$) then there are severe external MTL. This is the case with $0.0005\frac{m^3}{s}$.

At constant Q

$$ln(\frac{1}{1-X}) = \frac{k_c a_c L}{u} \tag{13}$$

$$\frac{L}{u} = \frac{V_{bed}/A_c}{Q/A_c} = \frac{W/\rho_{bed}}{Q} \tag{14}$$

$$ln(\frac{1}{1-X}) = -8.04 * 10^{-3} * 120 * \frac{4/500}{0.0005} \tag{15}$$

$$x = 100 \tag{16}$$

$$F_B = F_{A0} * X_A = C_{A0} * Q * X = 5 * 10^{-4} * 0.0005 * 1 = 2.5 * 10^{-7}\ \frac{mol}{s} \tag{17}$$

[3]:
```
X1=1-math.exp(-kc[0]*ac*W/(rhob*Q[0]))
FB1=CA0*Q[0]*X1

print("X1={0:.2f}".format(X1),'%')
print ("FB1={0:.8f}".format(FB1),'mol/s')
```

```
X1=1.00 %
FB1=0.00000025 mol/s
```

Answer to Q4

$$F_{A0}\frac{dX}{dW} = kC_{As} \tag{18}$$

for $Q = 0.05\ m^3/s$:

$$C_{As} = C_{Ab}\frac{k_c a_c}{k + k_c a_c} = 0.51 C_{Ab} \tag{19}$$

$$C_{Ab} = \frac{F_{A0}}{Q}(1-X) \tag{20}$$

at Q constant:

$$ln(\frac{1}{1-X}) = \frac{k * W * 0.51}{Q} \tag{21}$$

Here, k has units $\frac{m^3_{fl}}{s*kg_{cat}}$

given $k = 8\frac{m^3_{fl}}{m^3_{bed}*s} * \frac{1[m^3_{bed}]}{500[kg_{cat}]}$

$$ln(\frac{1}{1-X}) = \frac{8*4*0.51}{0.05*500} \tag{22}$$
$$X = 48 \tag{23}$$

$F_B = F_{A0}X = C_{A0}QX = 5*10^{-4}*0.05*0.48 = 1.2*10^{-5}\frac{mol}{s}$

[4]:
```
X2=1-math.exp(-k*W*CAs_coef[1]/(rhob*Q[1]))
FB2=CA0*Q[1]*X2

print("X2={0:.3f}".format(X2),'%')
print ("FB2={0:.7f}".format(FB2),'mol/s')
```

```
X2=0.477 %
FB2=0.0000119 mol/s
```

Answer to Q5

In the cases affected by MTL

External MTL is present when Q and hence F_{A0} are lower values, so the fluid spends more time in the reactor and higher conversion, X, is achieved. $k_c a_c << k$, Slow diffusion and fast reaction. So observed reaction rate = rate of external diffusion.

At high Q, when there are no MTL, even at low X, F_B is the highest.

$Q = 15m^3/s$ gives the highest F_B, $Q = 0.05m^3/s$ gives a slightly smaller value for F_B while having a larger conversion $X = 48$ So case $Q = 0.05m^3/s$ is perfect to produce the highest exit F_B yet higher conversion.

Answer to Q6

Diffusivities in liquid phase are lower (because of higher density), so liquid phase reactions are more prone to MTL. Lower diffusivities give lower Re and hence higher concentration, C_A, which means more MTL.

$kc \propto D_{AB}$ Therefore smaller D_{AB} results in smaller k_c or smaller mass transfer coefficient. The smaller mass transfer coefficient, the more prone the reaction is to mass transfer limitations. Since liquids have low diffusion rate, so they have higher MTL .