

ChE445_Seminar9_Winter2020_Solution

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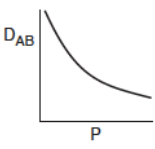
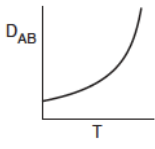
1 Seminar 9. External mass transfer limitations

Q1. Based on Example 14-4 from the textbook (Fogler's, 5th Ed.)

An externally mass-transfer limited reaction (gas-phase reaction mixture) is carried out in an isothermal packed-bed reactor with no pressure drop at a constant volumetric flow rate. At 400°C, conversion of 85% is achieved.

As a known rule of thumb, chemical reaction rate doubles at every 10-degree temperature increase (the exact increase must be found from Arrhenius law). To ensure full conversion, it was proposed to increase temperature to 430°C. Analyze the suggestion.

TABLE 11-2. DIFFUSIVITY RELATIONSHIPS FOR GASES, LIQUIDS, AND SOLIDS

<p>It is important to know the magnitude and the T and P dependence of the diffusivity</p> <div style="display: flex; align-items: center;">  <div style="margin-left: 10px;"> <p>Gas:</p> <p>D_{AB}</p> <p>P</p> </div> </div> <div style="margin-top: 20px;"> <p>Liquid:</p> <p>D_{AB}</p> <p>T</p>  </div>		Order of Magnitude		Temperature and Pressure Dependences ^a
	Phase	cm ² /s	m ² /s	
	Gas			
	Bulk	10 ⁻¹	10 ⁻⁵	$D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1) \frac{P_1}{P_2} \left(\frac{T_2}{T_1} \right)^{1.75}$
	Knudsen	10 ⁻²	10 ⁻⁶	$D_A(T_2) = D_A(T_1) \left(\frac{T_2}{T_1} \right)^{1/2}$
	Liquid	10 ⁻⁵	10 ⁻⁹	$D_{AB}(T_2) = D_{AB}(T_1) \frac{\mu_1}{\mu_2} \left(\frac{T_2}{T_1} \right)$
	Solid	10 ⁻⁹	10 ⁻¹³	$D_{AB}(T_2) = D_{AB}(T_1) \exp \left[\frac{E_D}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right]$

^a μ_1, μ_2 , liquid viscosities at temperatures T_1 and T_2 , respectively; E_D , diffusion activation energy.

Answer to Q1.

Case1: $T = 400^\circ\text{C}$, $X = 0.85$

Case2: $T = 430^\circ\text{C}$, $X = ?$

For a constant density system,

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{u} L \quad (\text{external MTL}) \quad (1)$$

for $T_{0,1}$ and $T_{0,2}$:

$$(*) \frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \frac{u_1}{u_2} \quad (\text{same } a_c \text{ and } L) \quad (2)$$

k_c and u depends on T^0 for the same conditions (except T^0): $F_{T01} = F_{T02}$ and $P_0 = \text{constant}$.

from ideal gas law:

$$F_{T0} = Q_{01} \frac{P_0}{R * T_{0,1}} = Q_{02} \frac{P_0}{R * T_{0,2}} \quad (3)$$

$$(4)$$

The pressure remains constant so

$$\frac{Q_{01}}{T_1} = \frac{Q_{02}}{T_2} \quad (5)$$

$$Q_0 = A_c [m^2] * u [m/s] \quad (6)$$

$$\frac{u_1}{T_1} = \frac{u_2}{T_2} (\text{same } a_c) \quad (7)$$

$$\frac{k_{c2}}{k_{c1}} = ? \quad (8)$$

$$k_c \propto \frac{u^{1/2} D_{AB}^{2/3}}{D_P^{1/2} \nu^{1/6}} \quad (9)$$

Taking the ratio of case 2 to case 1 and realizing that the particle diameter is the same for both cases gives us.

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{u_2}{u_1}\right)^{1/2} \left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3} \left(\frac{\nu_1}{\nu_2}\right)^{1/6} \quad (10)$$

The gas-phase diffusivity is a function of temperature (from Table 11-2)

$$D_{AB} \propto T^{1.75} \quad (11)$$

For most gases, viscosity increases with increasing temperature according to the following relation

From the ideal gas law : $P * Q = F * R * T$,

$$\rho[\dot{m}/Q] \propto T^{-1}$$

For gases we assume that the power-law is valid and $\mu \propto T^{2/3}$ see power-law viscosity law:
https://www.cfd-online.com/Wiki/Power-law_viscosity_law

$$\text{So } \nu = \frac{\mu}{\rho} \propto T^{5/3}$$

$$\nu = \frac{\mu}{\rho} \propto T^{3/2}$$

Combine into (*):

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{u_1 k_{c2}}{u_2 k_{c1}} = \frac{u_1}{u_2} \left(\frac{u_2}{u_1}\right)^{1/2} \left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3} \left(\frac{\nu_1}{\nu_2}\right)^{1/6} \quad (12)$$

$$= \left(\frac{T_1}{T_2}\right)^{0.5} * \left(\left(\frac{T_2}{T_1}\right)^{1.75}\right)^{2/3} * \left(\left(\frac{T_1}{T_2}\right)^{5/3}\right)^{1/6} = \left(\frac{T_2}{T_1}\right)^{0.39} = \left(\frac{703}{673}\right)^{0.39} = 1.02 \quad (13)$$

At $T_1 = 673 \text{ K}$, $\ln \frac{1}{1-X_1} = 1.897$ where $X_1 = 85\%$

$$\text{so } \ln \frac{1}{1-X_2} = 1.897 * 1.02 = 1.935$$

$X_2 = 0.855$ practically didn't change with 30°C increase of temperature.

Analysis: Consequently, conversion in an externally mass-transfer limited (MTL) process is not (almost) affected by T_0 as opposed to the intrinsic reaction rate. By increasing the temperature from 400°C to 430°C the conversion increases by only 2.19% from 0.85 to 0.87.

```
[47]: import math
X1=0.85
T1=273+400
T2=273+430
ratio=pow(T2/T1,0.39)
lninvx1=math.log(1/(1-X1))
X2=1-math.exp(-1*ratio*lninvx1)
print("X2={0:.3f}".format(X2))
print(" (1/(1- X1))=",lninvx1)
#print ("Increase in conversion by increasing temperature={0:.3f}".format(((0.869-0.85)/0.869)*100))
```

$$X2=0.855$$

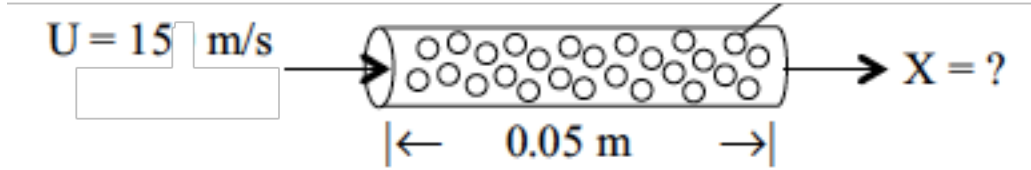
$$(1/(1- X1))= 1.8971199848858813$$

Q2. Based on Example 14-2 from the textbook (Fogler's, 5th Ed.)

Hydrazine decomposition to nitrogen and hydrogen N_2H_4 . In a proposed study, a 2% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles with The volume-average partcel diameter of $3.6 * 10^{-3}$ at a gas-phase velocity of 15m/s and a temperature of 750K . The kinematic viscosity of helium at this temperature is $4.5 * 10^{-4}\text{m}^2/\text{s}$. The hydrazine decomposition reaction is believed to be externally mass transfer-limited under these conditions. If the packed bed is 0.05m in length, what conversion can be expected? Assume isothermal operation.

$$D_{AB} = 0.69 * 10^{-4} \text{ m}^2/\text{s at } 298 \text{ K}$$

Bed porosity: 30%



Answer to Q2.

For a constant-density system when the process is limited by external MTL:

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{u} L \quad (14)$$

$$a_c = \frac{6(1-\phi)}{D_p} = \frac{6 * 0.7}{3.6 * 10^{-3}} = 1167 \left[\frac{m^2}{m^3} \right] \quad (15)$$

$$k_c = \frac{D_{AB} * Sh}{D_p} \quad (16)$$

D_{AB} at 750? See the table in Q1.

$$D_{N_2H_4} \text{ (at 750)} = D_{298} \left(\frac{750}{298} \right)^{1.75} = 3.47 * 10^{-4} \frac{m^2}{s}$$

Frossling correlation:

$$Sh = 2 + 0.6 * Re^{1/2} Sc^{1/3} \quad (17)$$

$$Re(p) = \frac{u_s * D_p * \rho_{fluid}}{\mu_{fluid}} = \frac{u_s * D_p}{\nu_{fluid}} = \frac{15 * 3.6 * 10^{-3}}{4.5 * 10^{-4}} = 120 \quad (18)$$

$$Sc = \frac{\nu}{D_{AB}} = \frac{4.5 * 10^{-4}}{3.47 * 10^{-4}} = 1.3 \quad (19)$$

$$Sh = 2 + 0.6 * (120)^{0.5} (1.3)^{1/3} = 9.2 \quad (20)$$

$$k_c = \frac{Sh * D_{AB}}{D_P} = \frac{9.2 * 3.47 * 10^{-4}}{3.6 * 10^{-3}} = 0.89 [m/s] \quad (21)$$

Then $X = 1 - \exp\left[\frac{-k_c * a_c * L}{u}\right] = 0.97$ where $L = 5 \text{ cm}$

[26]: `import math`

```

T=750
Dp=3.6*pow(10,-3) #m
phi=0.3
ac=6*(1-phi)/Dp
L=0.05 #m
us=15
nu=4.5*pow(10,-4) #m^2/s
Rep=us*Dp/nu
DAB=0.69*pow(10,-4)*pow(T/298,1.75)
Sc=nu/DAB
Sh=2+0.6*pow(Rep,0.5)*pow(Sc,1/3)
kc=Sh*DAB/Dp
X=1-math.exp(-kc*ac*L/us)

print ("DAB={0:.3f}".format(DAB))
print ("Re={0:.3f}".format(Rep))
print ("Sc={0:.3f}".format(Sc))
print ("Sh={0:.3f}".format(Sh))
print ("kc={0:.3f}".format(kc))
print ("X={0:.3f}".format(X))

```

```

max DAB=0.000
max Re=120.000
max Sc=1.297
max Sh=9.168
max kc=0.884
max X=0.968

```