

ChE445_Seminar10_Winter2020-Solution

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1 Seminar 10. Isothermal effective diffusivity. Internal effectiveness factor.

Q1. Calculation of effective diffusivity.

From “Introduction to Chemical Reactor Analysis”, R.E. Hayes, J.P. Mmbaga, 2nd Ed. CRC Press.

Calculate effective diffusivity for methane in air at $500K$ and $120kPa$ in a catalyst with a porosity of 0.4 (uniform pore distribution), pellet density of $1,400 \frac{kg}{m^3}$ and a BET surface area of $180,000 \frac{m^2}{kg}$. Assume tortuosity factor of 4.

Values for diffusion volumesome values, i , for some molecules:

H2	7.07	CO	18.9
N2	17.9	CO2	26.9
O2	16.6	H2O	12.7
air	20.1	NH3	14.9
CH4	24.42	He	2.88
Ar	16.1	N2O	35.9

Answer to Q1.

$$T = 500K$$

$$M_A(CH_4) = 16 \frac{g}{mol}$$

$$M_B(air) = 29 \frac{g}{mol}$$

$$P = 120000pa$$

$$\nu_A(CH_4) = 24.42$$

$$\nu_B(air) = 20.1$$

Binary molecular diffusion in gases $[m^2/s]$ can be calculated using the Fuller formula

(P –pressure in $[Pa]$, T – temperature in $[K]$, M – molar mass in $[g/mol]$, ν_i is a diffusion volume.):

$$D_{AB} = \frac{1.013 * 10^{-2} * T^{1.75} (\frac{1}{MA} + \frac{1}{MB})^{0.5}}{P * ((\sum \nu_i)_A^{1/3} + (\sum \nu_i)_B^{1/3})^2} = \frac{1.013 * 10^{-2} * 500^{1.75} (\frac{1}{16} + \frac{1}{29})^{0.5}}{120000 * (24.42^{1/3} + 20.1^{1/3})^2} = 4.4 * 10^{-5} \frac{m^2}{s} \quad (1)$$

Which is a reasonable number for a gas phase.

Knudsen diffusivity D_K for gas species varies with the pore diameter d_p in $[m]$, T the temperature in $[K]$, and the molar mass of the diffusion species, M , in $[g/mol]$.

We can calculate d_p from the following equation:

(ϕ_P – pellet porosity, S – catalyst surface area in $[\frac{m^2}{kg}]$ (for example, from BET measurements) ρ – pellet density in $[\frac{kg}{m^3}]$.)

$$d_p = \frac{4 * \phi_p}{S * \rho} = \frac{4 * 0.4}{180000 [\frac{m^2}{kg}] * 1400 [\frac{kg}{m^3}]} = 6.35 * 10^{-9} [m] \quad (2)$$

$$(3)$$

The equivalent pore diameter is taken as the average diameter of the pores in the pellet, which gives a reasonable approximation provided that there is a relatively narrow pore size distribution.

The Knudsen diffusion coefficient, D_k in $[m^2/s]$ in a straight round pore can be calculated from the following formula: ($M = 16 \frac{g}{mol}$ molecular mass of the diffusing species.)

$$D_k = 48.5 * d_p * (\frac{T}{M})^{0.5} = 48.5 * 6.35 * 10^{-9} * (\frac{500}{16})^{0.5} = 1.72 * 10^{-6} \frac{m^2}{s} \quad (4)$$

D_{pore} is diffusivity in a pore, which is a combination of molecular and Knudsen diffusivity. In general, the concentration dependence of the pore diffusion coefficient is not large, and in many cases, the following equation (Bosanquet formula) is used to compute the pore diffusion coefficient.

$$D_{pore} = (\frac{1}{D_{AB}} + \frac{1}{D_K})^{-1} = 1.66 * 10^{-6} \frac{m^2}{s} \quad (5)$$

Therefore, it is governed mostly by D_k because of small pore size (width).

Effective diffusivity in a catalyst for unimodal pore size distribution, D_{eff} :

(ϕ_p – pellet porosity, τ – tortuosity factor, typically 3 – 4, for calculation example refer to Fogler, Elements of CRE, example 12-1 page 817)

$$D_{eff} = \frac{\phi_p D_{pore}}{\tau} = \frac{0.4 * 1.66 * 10^{-6}}{4} = 1.66 * 10^{-7} \frac{m^2}{s} \quad (6)$$

Note that D_{eff} is 265 times lower than bulk diffusivity D_{AB} and D_{eff} does not depend on catalyst particle size.

FYI: When a catalyst pellet has two distinct regions of pore sizes (for example, micro or meso pores inside an individual catalyst grain and macro pores between catalyst grains pressed into a catalyst pellet), then effective diffusivity is:

$$D_{eff} = D_{pore,M} \phi_{p,M}^2 + \left[\frac{\phi_{p,Micro}^2 (1 + 3\phi_{p,M})}{(1 - \phi_{p,M})} \right] D_{pore,micro} \quad (7)$$

Where M refers to a large - pore region and “micro” - to a smaller pore region. In each of these regions that diffusivities can be calculated using the previously mentioned equations and corresponding ϕ_p .

```
[1]: import math
T=500
MA=16 #g/mol
MB=29 #g/mol
P=120000#
nuA=24.42
nuB=20.1
phi_p=0.4 #pellet porosity
S=180000 #catalyst surface area
rho=1400 #pellet density
R=8.314 #J/mol/K
tau=4 #tortuosity factor
dp=4*phi_p/(S*rho) #m
DAB=(1.013*pow(10,-2)*pow(T,1.75)*pow((1/MA+1/MB),0.5))/(P*pow(pow(nuA,1/
↪3)+pow(nuB,1/3),2))
#Dk=(dp/3)*pow(((8*R*T)/(3.14*MA*0.01)),0.5)
Dk=48.5*dp*pow((T/(MA)),0.5)
Dpore=pow((1/DAB+1/Dk),-1)
Deff=(phi_p*Dpore)/tau
print("DAB={0:.6f}".format(DAB),'bulk diffusivity [m2/s]')
print("dp={0:.10f}".format(dp),'m')
print("Dk={0:.8f}".format(Dk),'Knudsen diffusivity [m2/s]')
print("Dpore={0:.8f}".format(Dpore),'m2/s')
print("Deff={0:.9f}".format(Deff),'m2/s')
print("DAB/Deff={0:.1f}".format(DAB/Deff))
```

```
DAB=0.000044 bulk diffusivity [m2/s]
dp=0.0000000063 m
Dk=0.00000172 Knudsen diffusivity [m2/s]
Dpore=0.00000166 m2/s
Deff=0.000000166 m2/s
DAB/Deff=265.6
```

Q2. Calculation of generalized Thiele modulus and internal effectiveness factor

A heterogeneous catalytic reaction follows a Langmuir-Hinshelwood mechanism but under certain conditions the L-H rate law can be simplified to a first-order power law as $r = kC_A$. Specific surface area of catalyst: $100[\frac{m^2}{g}]$, effective diffusivity: $0.02[\frac{cm^2}{s}]$ (or $[\frac{cm^3 fluid}{cm catalyst * s}]$), intrinsic rate constant: $2.8 * 10^{-7}[\frac{m^3 fluid}{m^2 catalyst * s}]$ (or $[\frac{m}{s}]$). The reaction is in gas-phase, process T is $500[K]$, partial pressure of A is $0.24 [MPa]$, compressibility factor is 0.8 , catalyst bed density is $1.2 * 10^6[\frac{g}{m^3 bed}]$ (independent of the particle size), bed porosity is 0.4 .

There are no external mass transfer limitations under all conditions of this problem. Assume an isothermal pellet.

2a). Consider $1.5[mm]$ (radius) spherical catalyst particles. Find generalized Thiele modulus, internal effectiveness factor and observed reaction rate as $[\frac{mol}{m^2 catalyst surface area * s}]$, $[\frac{mol}{m^3 bed * s}]$ and as $[\frac{mol}{m^2 external catalyst surface area * s}]$.

2b). What should be the particle size to avoid internal mass transfer limitations?

Answer to Q2

2a) There are no external mass transfer limitations under all conditions of this problem. In this case, for a 1^{st} order reaction for sphere, ϕ_n is (refer to Fogler, Elements of CRE, 5th Ed. page 732):

$$\phi_n = \frac{R}{3} \left(\frac{k}{D_{eff}} \right)^{0.5} \quad (8)$$

The Thiele modulus, ϕ_n , will always contain a subscript (e.g., n), which refers to the reaction order. ϕ_n is a measure of the ratio of “a” surface reaction rate to “a” rate of diffusion through the catalyst pellet. Here k is a catalyst-volume based constant (intrinsic).

$$r[\frac{mol}{m_{cat}^3 \cdot s}] = k * C_A[\frac{mol}{m^3 fluid}] \quad (9)$$

We are given k as $[\frac{m_{fl}^3}{m_{cat}^2 \cdot s}] (= [m/s])$.

$$k[\frac{m_{fl}^3}{m_{cat}^3 \cdot s}] = k''[\frac{m_{fl}^3}{m_{cat}^2 \cdot s}] * SSA[\frac{m_{cat}^2}{g_{cat}}] * \rho_c[\frac{g_{cat}}{m_{cat}^3}] \quad (10)$$

$$\rho_c = \frac{\rho_{bed}[\frac{g_{cat}}{m_{bed}^3}]}{1 - \Phi}; \quad \Phi = \text{the porosity of the bed}[\frac{m_{cat}^3}{m_{bed}^3}] \quad (11)$$

$$k = 2.8 * 10^{-7} * 100 * \frac{1.2 * 10^6}{1 - 0.4} = 56[\frac{m_{fl}^3}{m_{cat}^3 \cdot s}] \quad (12)$$

$$\phi_n = \text{Thiele modulus} = \frac{0.0015}{3} \left(\frac{56}{0.02 * 10^{-4}} \right)^{0.5} = 2.6 \quad (13)$$

$$\eta = \frac{\text{observed rate}}{\text{intrinsic rate at surface conditions}} = \frac{\tanh \phi_n}{\phi_n} = 0.37 \quad (14)$$

Since we do not have external limitations, surface conditions $C_{As}, T_s = \text{bulk conditions } C_{Ab}, T_b$.

Intrinsic rate: rate from rate law (Assume an isothermal pellet)

$$r'' = k'' * C_A \quad (15)$$

Gas phase:

$$P * V = Z * N * R * T \quad (16)$$

$$C_A = \frac{N_A}{V} = \frac{P_A}{Z * R * T} = \frac{0.24 * 10^6}{0.8 * 8.314 * 500} = 72 \left[\frac{\text{mol}}{\text{m}_{fl}^3} \right] \quad (17)$$

$$r'' = k'' * C_A = 2.8 * 10^{-7} \left[\frac{\text{m}_{fl}^3}{\text{m}_{cat}^2 \cdot s} \right] * 72 \frac{\text{mol}}{\text{m}_{fl}^3} = 2 * 10^{-5} \left[\frac{\text{mol}}{\text{m}_{cat}^2 * s} \right] \quad (18)$$

$$\text{Observed rate} = \eta * \text{intrinsic rate} = 0.37 * 2 * 10^{-5} = 0.74 * 10^{-5} \left[\frac{\text{mol}}{\text{m}_{cat}^2 \cdot s} \right]$$

FYI: same refers to rate constant: observed rate constant = $\eta * \text{intrinsic rate constant}$ (no external MTL) or if there are external MTL/HTL then intrinsic rate constant at T_s .

Observed rate in $\left[\frac{\text{mol}}{\text{m}_{bed}^3 * s} \right]$?

connect to bed volume:

$$r \left[\frac{\text{mol}}{\text{m}_{bed}^3 * s} \right] = r'' \left[\frac{\text{mol}}{\text{m}_{cat}^2 \cdot s} \right] * SSA \left[\frac{\text{m}_{cat}^2}{\text{g}_{cat}} \right] * \phi_{bed} \left[\frac{\text{g}_{cat}}{\text{m}_{bed}^3} \right] = 0.74 * 10^{-5} * 100 * 1.2 * 10^6 = 888 \left[\frac{\text{mol}}{\text{m}_{bed}^3 \cdot s} \right]$$

In units of $\left[\frac{\text{mol}}{\text{m}_{\text{external catalyst surface area}}^2 \cdot s} \right]$?

Let's use m_{bed}^3 and $a_c = \left[\frac{\text{m}_{ext surf area}}{\text{m}_{bed}^3} \right]$

$$a_c(\text{sphere}) = \frac{6(1 - \phi)}{D_p} \quad (19)$$

external area \neq total (internal pores + external)

$$r'' \left[\frac{\text{mol}}{\text{m}_{ext area * s}^2} \right] = r \left[\frac{\text{mol}}{\text{m}_{bed}^3 * s} \right] / a_c \left[\frac{\text{m}_{ext}^2}{\text{m}_{bed}^3} \right] = \frac{888 * 0.003}{6 * (1 - 0.4)} = 0.74 \left[\frac{\text{mol}}{\text{m}_{\text{external catalyst surface area}}^2 \cdot s} \right] \quad (20)$$

```
[2]: import math
import numpy as np
T=500
Dp=0.003
R=8.314
z=0.8
kp=2.8*pow(10,-7)
SSA=100
phi=0.4
P_A=0.24*pow(10,6)
rho_bed=1.2*pow(10,6)
rho_c=rho_bed/(1-phi)
r=0.0015
D_eff=0.02*pow(10,-4)
k=kp*SSA*rho_c
phi_n=(r/3)*pow((k/D_eff),0.5)
eta=np.tanh(phi_n)/phi_n
CA=P_A/(z*R*T)
rp=kp*CA
Intr_rate=2*pow(10,-5)
robs=eta*Intr_rate
phi_bed=1.2*pow(10,6)
rate=robs*SSA*phi_bed
a_c=(6.*(1-phi))/Dp
rp2=rate/a_c
print("k={0:.0f}".format(k), '[m^3_{fl}]/m^3_{cat}/s')
print("robs={0:.6f}".format(robs), '[mol/m^2_{cat}]/s')
print("rate={0:.3f}".format(rate), '[mol/m^3_{bed}]/s')
print("phi_n={0:.3f}".format(phi_n))
print("eta={0:.3f}".format(eta))
print("rp2={0:.3f}".format(rp2), '[mol\m^2_{external catalyst surface area}]/s')
```

```
k=56 [m^3_{fl}]/m^3_{cat}/s
robs=0.000007 [mol/m^2_{cat}]/s
rate=898.027 [mol/m^3_{bed}]/s
phi_n=2.646
eta=0.374
rp2=0.748 [mol\m^2_{external catalyst surface area}]/s
```

Q2-2b.

To avoid internal MTL, $\eta \geq 0.95$

$$0.95 = \eta = \frac{\tanh \Phi_n}{\Phi_n} \quad (21)$$

$$\Phi_n = 0.4$$

$$\Phi_n[sphere\ 1^{st}\ order\ rxn] = \frac{R}{3} \left(\frac{k}{D_{eff}} \right)^{0.5} \quad (22)$$

k and D_{eff} do not depend on particle size (only on T^0)

$$R = 0.4 * 3 * \left(\frac{0.02 * 10^{-4}}{56} \right)^{0.5} = 0.21 mm$$

Particles of this size and smaller are free of internal MTL.

```
[12]: import numpy as np
from scipy.optimize import fsolve

def f(x):
    return (np.tanh(x)/x)-0.95

x = fsolve(f,0.1)
f(x)

print('phi_n=',x)

phi=0.4
Deff=0.02*pow(10,-4)
k=56          #[m~3_{fl}]/m~3_{cat}/s]
R=pow(phi*3.*(Deff/k),0.5)

print("R={0:.6f}".format(R), 'm')
```

```
phi_n= [0.39945811]
R=0.000207 m
```
