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CH EN 3553

Homework 8

1.a) $\sigma_1 = \sigma_2 = \sigma_3 = \sigma_4 = 1 \Rightarrow$

$I + W \rightarrow TBA$

$r = \frac{r_I}{\nu_I} = \frac{r_I}{-1} \Rightarrow r = -r_I$; step 3 is rate limiting $\Rightarrow r = r_3 = -r_I$

$$r_3 = k_3 [W\cdot S] \frac{[I\cdot S]}{C_T} - k_{-3} [TBA\cdot S] \frac{[S]}{C_T}$$

steps 1, 2, & 4 are QE:

r_1: $k_1 [I][S] = k_{-1} [I\cdot S] \Rightarrow [I\cdot S] = K_1 [I][S]$

r_2: $k_2 [W][S] = k_{-2} [W\cdot S] \Rightarrow [W\cdot S] = K_2 [W][S]$

r_4: $k_4 [TBA\cdot S] = k_{-4} [TBA][S] \Rightarrow [TBA\cdot S] = \frac{k_{-4}}{k_4} [TBA][S] = K_{TBA} [TBA][S]$

$C_T = [S] + [I\cdot S] + [W\cdot S] + [TBA\cdot S] \Rightarrow$

$C_T = [S] + K_1 [I][S] + K_2 [W][S] + K_{TBA} [TBA][S] \Rightarrow$

$$[S] = \frac{C_T}{1 + K_1 [I] + K_2 [W] + K_{TBA} [TBA]} \Rightarrow$$

$$r_3 = \frac{k_3 K_2 (W)(S) K_1 (I)(S)}{C_T} - \frac{k_{-3} K_{TBA} (TBA)(S)(S)}{C_T}$$

$$r_3 = \frac{k_3 K_1 K_2 (I)(W)(S)^2}{C_T} - \frac{k_{-3} K_{TBA} (TBA)(S)^2}{C_T}$$

$$r_3 = \frac{k_3 K_1 K_2 (I)(W) C_T}{(1 + K_1 (I) + K_2 (W) + K_{TBA}(TBA))^2} - \frac{k_{-3} K_{TBA} (TBA) C_T}{(1 + K_1 (I) + K_2 (W) + K_{TBA}(TBA))^2}$$

$$\boxed{-r_I = C_T \left(k_3 K_1 K_2 [I][W] - k_{-3} K_{TBA} [TBA]\right)\left(1 + K_1 [I] + K_2 [W] + K_{TBA} [TBA]\right)^{-2}}$$

b) Step 1 is rate limiting $\Rightarrow r = r_1 = -r_I$

$r_1 = k_1(I)(S) - k_{-1}(I\cdot S)$

Steps 2, 3, + 4 are QE:

$r_2: k_2(W)(S) = k_{-2}(W\cdot S) \Rightarrow (W\cdot S) = K_2(W)(S)$

$r_3: \dfrac{k_3(W\cdot S)(I\cdot S)}{C_T} = \dfrac{k_{-3}(TBA\cdot S)(S)}{C_T} \Rightarrow (I\cdot S) = \dfrac{(TBA\cdot S)(S)}{K_3(W\cdot S)}$

$r_4: k_4(TBA\cdot S) = k_{-4}(TBA)(S) \Rightarrow (TBA\cdot S) = K_{TBA}(TBA)(S)$

$C_T = (S) + (I\cdot S) + (W\cdot S) + (TBA\cdot S) \Rightarrow$

$C_T = (S) + \dfrac{(TBA\cdot S)(S)}{K_3(W\cdot S)} + K_2(W)(S) + K_{TBA}(TBA)(S) \Rightarrow$

$C_T = (S) + \dfrac{K_{TBA}(TBA)(S)^2}{K_3K_2(W)(S)} + K_2(W)(S) + K_{TBA}(TBA)(S) \Rightarrow$

$(S) = \dfrac{C_T}{1 + \dfrac{K_{TBA}(TBA)}{K_2K_3(W)} + K_2(W) + K_{TBA}(TBA)} \Rightarrow$

$r_1 = k_1(I)(S) - k_{-1}(I\cdot S) = k_1(I)(S) - \dfrac{k_{-1}(TBA\cdot S)(S)}{K_3(W\cdot S)} =$

$(S)\left[k_1(I) - \dfrac{k_{-1}K_{TBA}(TBA)}{K_2K_3(W)}\right] \Rightarrow$

$$\boxed{-r_I = \left(\dfrac{C_T}{1 + \dfrac{K_{TBA}[TBA]}{K_2K_3[W]} + K_2[W] + K_{TBA}[TBA]}\right)\left(k_1[I] - \dfrac{k_{-1}K_{TBA}[TBA]}{K_2K_3[W]}\right)}$$

c) step 2 is rate limiting $\Rightarrow r = r_2 = -r_I$

$r = k_2 (I \cdot S)(W) - k_{-2}(TBA \cdot S)$

steps 1 + 3 are QE :

$r_1 : k_1(I)(S) = k_{-1}(I \cdot S) \Rightarrow (I \cdot S) = K_1(I)(S)$

$r_3 : k_3 (TBA \cdot S) = k_{-3}(TBA)(S) \Rightarrow (TBA \cdot S) = K_{TBA}(TBA)(S)$

$C_T = (S) + (I \cdot S) + (TBA \cdot S) = (S) + K_1(I)(S) + K_{TBA}(TBA)(S) \Rightarrow$

$(S) = \dfrac{C_T}{1 + K_1(I) + K_{TBA}(TBA)} \Rightarrow$

$r = k_2 K_1 (I)(S)(W) - k_{-2} K_{TBA}(TBA)(S) \Rightarrow$

$$\boxed{-r_I = \left(k_2 K_1 [I][W] - k_{-2} K_{TBA}[TBA]\right)\left(\frac{C_T}{1 + K_1[I] + K_{TBA}[TBA]}\right)}$$

d) Step 3 is rate limiting $\Rightarrow r = r_3 = -r_I$

$r = k_3(I\cdot S_1)(W\cdot S_2) - k_{-3}(TBA)(S_1)(S_2)$

Steps 1+2 are QE:

$r_1: k_1(I)(S_1) = k_{-1}(I\cdot S_1) \Rightarrow (I\cdot S_1) = K_1(I)(S_1)$

$r_2: k_2(W)(S_2) = k_{-2}(W\cdot S_2) \Rightarrow (W\cdot S_2) = K_2(W)(S_2) \Rightarrow$

$r = k_3 K_1 K_2 (I)(W)(S_1)(S_2) - k_{-3}(TBA)(S_1)(S_2)$

$C_{T,1} = (S_1) + (I\cdot S_1) = (S_1) + K_1(I)(S_1) \Rightarrow (S_1) = \dfrac{C_{T,1}}{1+K_1(I)}$

$C_{T,2} = (S_2) + (W\cdot S_2) = (S_2) + K_2(W)(S_2) \Rightarrow (S_2) = \dfrac{C_{T,2}}{1+K_2(W)} \Rightarrow$

$$\boxed{-r_I = \left(k_3 K_1 K_2 [I][W] - k_{-3}[TBA]\right)\left(\frac{C_{T,1}}{1+K_1[I]}\right)\left(\frac{C_{T,2}}{1+K_2[W]}\right)}$$

2. a) design equation: $W = F_{A0}\int_0^{X_A}\frac{dX_A}{-r_{AS}'} = C_{A0}\dot{V}\int_0^{X_A}\frac{dX_A}{k' C_{AS}}$

$W_A = k_c'(C_A - C_{AS})$

because we're operating at steady state $\Rightarrow W_A = -r_A'' \Rightarrow$

$k_c'(C_A - C_{AS}) = k' C_{AS} \Rightarrow C_{AS} = \frac{k_c' C_A}{k_c' + k'}$

$$Sh = \frac{k_c d_p}{D_{AB}} \Rightarrow k_c = \frac{D_{AB} Sh}{d_p} = \frac{100 D_{AB}\sqrt{Re}}{d_p} = \frac{100 D_{AB}}{d_p}\sqrt{\frac{\rho v D}{\mu}} = \frac{100 D_{AB}}{d_p}\sqrt{\frac{vD}{\nu}}$$

$$k_c = \frac{100(0.01\ cm^2/s)}{0.1\ cm}\sqrt{\frac{(10\ cm/s)(0.1\ cm)}{0.02\ cm^2/s}} = 70.71\ \frac{cm}{s}$$

$$k_c' = k_c a = \left(70.71\ \frac{cm}{s}\right)\left(60\ \frac{cm^2}{g\text{-}cat}\right) = 4242.64\ \frac{cm^3}{s \cdot g\text{-}cat}$$

$$C_{AS} = \frac{k_c' C_{A0}(1-X_A)}{k_c' + k'} \Rightarrow W = C_{A0}\dot{V}\int_0^{X_A}\frac{k_c' + k'}{k' k_c' C_{A0}(1-X_A)}dX_A \Rightarrow$$

$$W = \dot{V}\frac{k_c' + k'}{k_c' k'}\int_0^{X_A}\frac{dX_A}{1-X_A} = \left(10\frac{L}{s}\right)\left(\frac{4242.64\ \frac{cm^3}{s\cdot g\text{-}cat} + 0.01\ \frac{cm^3}{s\cdot g\text{-}cat}}{\left(4242.64\ \frac{cm^3}{s\cdot g\text{-}cat}\right)\left(0.01\ \frac{cm^3}{s\cdot g\text{-}cat}\right)}\right)\int_0^{X}\frac{dX}{1-X}$$

$$= (10^6\ g\text{-}cat)\int_0^{X}\frac{dX}{1-X} = (10^6\ g\text{-}cat)\left(-\ln(1-X)\Big|_0^{X_A}\right) = (10^6\ g\text{-}cat)[\ln(1) - \ln(1-X_A)]$$

$$= (10^6\ g\text{-}cat)(-\ln(1-0.60)) = \boxed{916.29\ kg\ catalyst}$$

b) $C_A = C_{A0}(1-X_A)\left(\frac{T_0}{T}\right)$ $\quad C_{AS} = \frac{k_c' C_A}{k_c' + k'}$ $\quad k'(T) = k_{300}'\exp\left(\frac{E_a}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$

$$W = C_{A0}\dot{V}\int_0^{X_A}\frac{dX_A}{k'\cdot\frac{k_c' C_A}{k_c' + k'}} = C_{A0}\dot{V}\int_0^{X_A}\frac{T(k_c' + k')dX_A}{k'\cdot k_c' C_{A0}(1-X_A)T_0} \Rightarrow$$

$$W = \frac{\dot{V}}{k_c' T_0}\int_0^{X_A}\frac{(k_c' + k')T}{k'(1-X_A)}dX_A$$

$$\cancel{\frac{dE}{dt}}^{0} = \cancel{\dot{Q}}^{0} - \cancel{\dot{W}_s}^{0} - F_{A0}\sum\Theta_i C_{pi}(T_i - T_0) - F_{A0}X_A\Delta H_{rxn} \Rightarrow$$

$$0 = (T - T_0)\sum\Theta_i C_{pi} + X_A\Delta H_{rxn}\ ;\ \sum\Theta_i C_{pi} = 1\left(25\frac{cal}{mol\cdot K}\right) + 1\left(75\frac{cal}{mol\cdot K}\right) =$$

$$100\ \frac{cal}{mol\cdot K} \Rightarrow 0 = (T - 300\ K)\left(100\ \frac{cal}{mol\cdot K}\right) + X_A\left(-10{,}000\ \frac{cal}{mol}\right) \Rightarrow$$

In [10]:

```
#imports
import numpy as np
from scipy.integrate import quad

#constant values
Ea=4000 #cal/mol
kp300=0.01 #cm^3/(s*g-cat)
R=1.987 #cal/(mol*K)
V̇=10 #L/s
V̇easyunits=V̇*1000 #cm^3/s
kcp=4242.64 #cm^3/(s*g-cat)
T0=300 #K

#defining function to integrate
def integrand(X):
    T=100*X+300 #K
    kp=kp300*np.exp(Ea/R*(1/300-1/T)) #cm^3/(s*g-cat)
    integrand=(kcp+kp)*T/(kp*(1-X)) #K
    return integrand

integral=quad(integrand,0,0.60) #K
constant=V̇easyunits/(kcp*T0) #g-cat/K
W=constant*integral[0]/1000 #kg-cat
print('W=',W,'kg-cat')
```

```
W= 538.0273375751698 kg-cat
```

$T = (100X_A + 300)$ K

$$W = \frac{\dot{v}}{k_c' T_0} \int_0^{X_A} \frac{(k_c' + k')T}{k'(1-X_A)} dX_A$$

$$k' = k'_{300} \exp\left(\frac{E_a}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$$

using the "quad" function from scipy.integrate in Python

$\Rightarrow$ $\boxed{W = 538.03 \text{ kg catalyst}}$