Homework V solution

Problem 1.

1. The reaction rate equations for the three reactions are as follow:

$$k_{b,1} = k_{f,1} / K_{C1}$$

$$k_{b,2} = k_{f,2} / K_{C2}$$

$$R_{r,1} = k_{f,1}[CO][H_2]^2 - k_{b,1}[CH_3OH]$$

$$R_{r,2} = k_{f,2}[CO][H_2O] - k_{b,2}[CO_2][H_2]$$

$$R_{r,3} = k_{f,3}[CH_3OH]$$

Note that you should consider backward reactions in the first two reactions.

2. The rates of formation of each species are as follow:

$$\frac{d[CO]}{dt} = -R_{r,1} - R_{r,2}$$

$$\frac{d[H_2]}{dt} = -2R_{r,1} + R_{r,2} + R_{r,3}$$

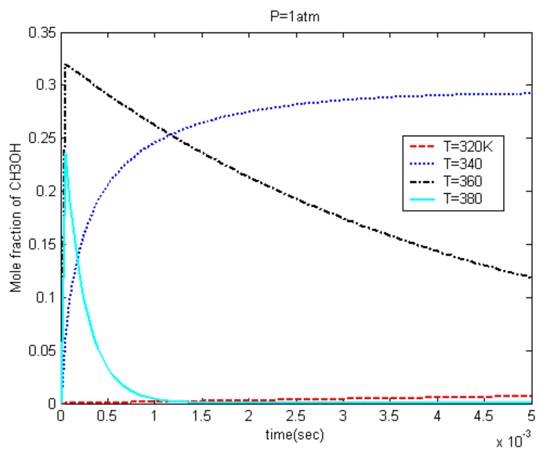
$$\frac{d[CH_3OH]}{dt} = R_{r,1} - R_{r,3}$$

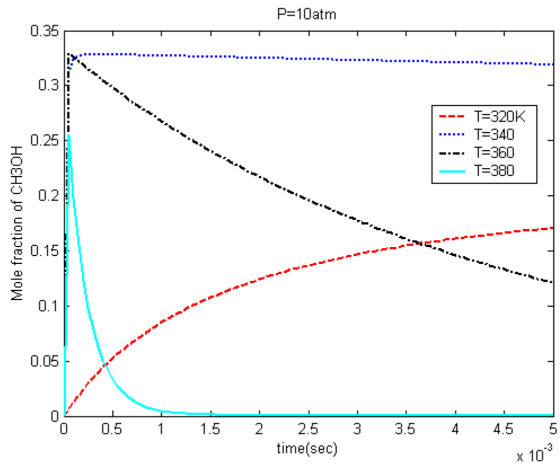
$$\frac{d[H_2O]}{dt} = -R_{r,2}$$

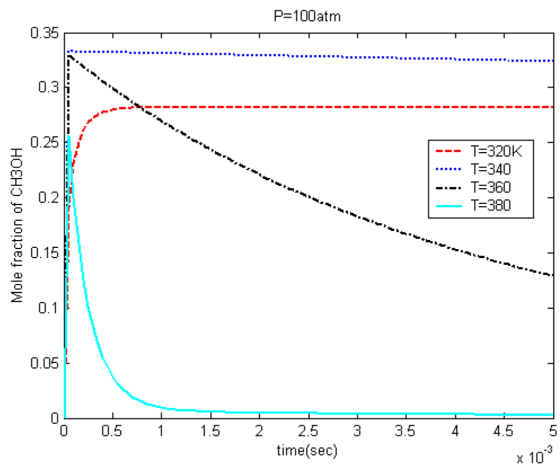
$$\frac{d[CO_2]}{dt} = R_{r,2}$$

$$\frac{d[CH_2O]}{dt} = R_{r,3}$$

3.







4. Increasing the pressure raises the mole fraction of CH3OH when $T \leq 340$, but does not have a significant effect after $T \geq 360$. It is due to the following reasons:

1) In the first reaction, which generates CH_3OH, the forward reaction favors higher pressure since the number of moles decreases during the forward reaction. Thus, by increasing the pressure of the reactor, the concentration of CH_3OH increases more rapidly.
2) After $T \geq 360$, even at low pressure, the first reaction is sufficiently fast. So increasing the pressure does not help. Also, note that the concentration of CH_3OH drops back to almost zero with time due to the third reaction (dissociation of CH3OH) indicating that the third reaction becomes active after $T \geq 360$.

5. The maximum mole fraction of CH_3OH one can obtain is ~33% at T=340K and P=10-100atm with a residence time less than 1msec.

6. The mole concentration changes at T=340K, P=10atm and residence time=1msec are as follow:

	CO	H_2	CH_3OH	H2O	CO_2	CH_2O	Total
Before the reactor (mol/m^3)	71.5	167	0	47.6	71.5	0	357.3
After the reactor (mol/m^3)	0.0	25.8	70.6	47.1	72.0	0.3	215.8

From the first law of the thermodynamics one can get Q as follow:

$$Q = H_2 - H_1 = \sum_P n_i \hat{h}_i - \sum_R n_i \hat{h}_i = -6.5\text{MJ}$$

Since this Q is with 357.3 mole of inlet mixture, one can get $\dot{Q}$ as follow:

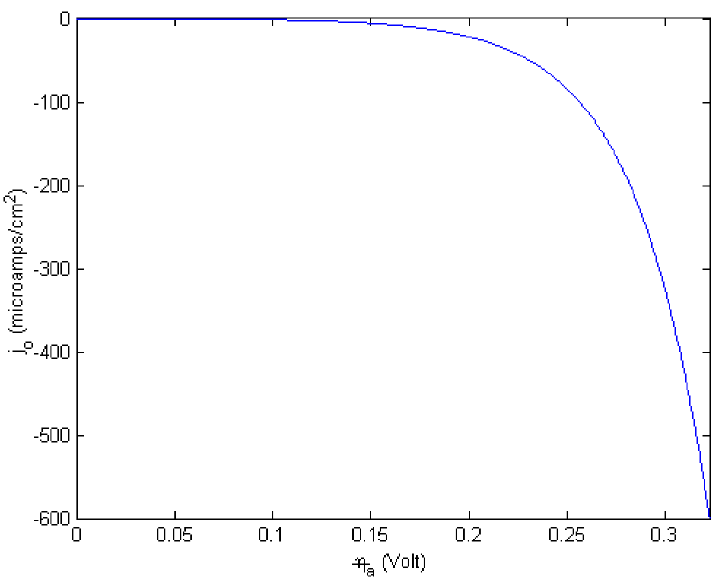
$$\dot{Q} = -6.5MJ / 357.3moles \cdot 300moles / s = -5.4Mwatt$$

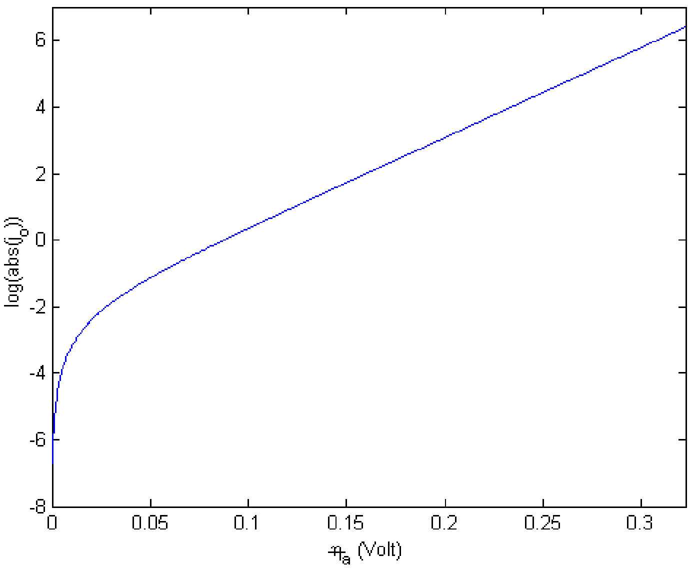
Problem 2.

1.

$$j_o = i_o / A = k^o [O]^* F = 10^{-6} cm/s \cdot 10^{-3} mol / 1000cm^3 \cdot 96485 Coulomb / mol = 9.65 \cdot 10^{-2} \mu A / cm^2$$

2 and 3. Using the Butler-Volmer equation, you can get the following figures





6
4
2
0
-2
-4
-6
-8
log(abs(j_o))
0
0.05
0.1
0.15
0.2
0.25
0.3
-η_a (Volt)