Homework V solution

Problem 1.

1. The reaction rate equations for the three reactions are as follow:
   \( k_{h,1} = k_{f,1} / K_{C_1} \)
   \( k_{h,2} = k_{f,2} / K_{C_2} \)
   \( R_{r,1} = k_{f,1} [CO][H_2] - k_{b,1} [CH_3OH] \)
   \( R_{r,2} = k_{f,2} [CO][H_2O] - k_{b,2} [CO_2][H_2] \)
   \( R_{r,3} = k_{f,3} [CH_3OH] \)
   Note that you should consider backward reactions in the first two reactions.

2. The rates of formation of each species are as follow:
   \( \frac{d[CO]}{dt} = -R_{r,1} - R_{r,2} \)
   \( \frac{d[H_2]}{dt} = -2R_{r,1} + R_{r,2} + R_{r,3} \)
   \( \frac{d[CH_3OH]}{dt} = R_{r,1} - R_{r,3} \)
   \( \frac{d[H_2O]}{dt} = -R_{r,2} \)
   \( \frac{d[CO_2]}{dt} = R_{r,2} \)
   \( \frac{d[CH_3O]}{dt} = R_{r,3} \)

3. 

![Graph showing the concentration of CH_3OH as a function of time and temperature.](image)
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 CH3OH, 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 CH3OH 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 CH3OH 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 CH3OH one can obtain is \( \sim 33\% \) at \( T=340K \) and \( P=10-100\text{atm} \) with a residence time less than 1msec.

6. The mole concentration changes at \( T=340K \), \( P=10\text{atm} \) and residence time=1msec are as follow:
<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>H₂</th>
<th>CH₃OH</th>
<th>H₂O</th>
<th>CO₂</th>
<th>CH₂O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before the reactor (mol/m³)</td>
<td>71.5</td>
<td>167</td>
<td>0</td>
<td>47.6</td>
<td>71.5</td>
<td>0</td>
<td>357.3</td>
</tr>
<tr>
<td>After the reactor (mol/m³)</td>
<td>0.0</td>
<td>25.8</td>
<td>70.6</td>
<td>47.1</td>
<td>72.0</td>
<td>0.3</td>
<td>215.8</td>
</tr>
</tbody>
</table>

From the first law of the thermodynamics one can get \( Q \) as follow:
\[
Q = H_2 - H_1 = \sum_{i} n_i \hat{h}_i - \sum_{f} n_f \hat{h}_f = -6.5 \text{MJ}
\]

Since this \( Q \) is with 357.3 mole of inlet mixture, one can get \( \dot{Q} \) as follow:
\[
\dot{Q} = -6.5 \text{MJ} / 357.3 \text{moles} \cdot 300 \text{moles/s} = -5.4 \text{Mwatt}
\]

**Problem 2.**

1. \( j_o = i_o / A = k^0 [O] \) \( F = 10^{-6} \text{cm/s} \cdot 10^{-3} \text{mol/1000cm}^3 \cdot 96485 \text{Coulomb/mol} = 9.65 \cdot 10^{-2} \mu \text{A/cm}^2 \)

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