Problem #1

In this problem, you will practice working with finite rate reaction equations in the context of synthetic fuel production. Review the ozone chemistry example in the note before working on this example. You will discover how operating conditions must be selected carefully to maximize the yield of the desired chemical while minimizing others.

A catalytic reactor is used for the synthesis of methanol, CH_3OH, starting with water and carbon monoxide that are produced from coal gasification. The catalyst in the reactor is active at temperatures between 300 and 450 K. The reactor runs at isothermal conditions. The important "elementary" reactions for the conversion of carbon monoxide and water to methanol are:

(1) $CO + 2H_2 \Leftrightarrow CH_3OH$
(2) $CO + H_2O \Leftrightarrow CO_2 + H_2$
(3) $CH_3OH \rightarrow H_2 + CH_2O$

While these are, in principle, not elementary reactions, for the purpose of this analysis they can be considered as if they were. These reactions take place in the gas phase, and under isothermal conditions. The first two reactions are reversible, the third in an irreversible dissociation of methanol that, if possible, should be avoided.

The feed gas into the reactor consists of 7/15 hydrogen, 1/5 carbon monoxide, 1/5 carbon dioxide and 2/15 steam, all by volume. The total molar flow rate is 300 mol/s, the inlet temperature of the feed gas ranges from 300 - 400 K, and the reactor pressure ranges from $1 - 160$ atm.

The objective of the following analysis is to find the conditions at which we can maximize the production of methanol within the reactor, including the pressure, temperature and residence time. The residence time is defined as the time the gas spends within the reactor to reach the final state. The following data are provided for the reactions:

$$K_{C1} = \frac{131667}{\exp\left[\dfrac{-30620}{R}\left(\dfrac{1}{T} - \dfrac{1}{298}\right)\right]}(0.001987T)^2\left(\frac{m^3}{mol}\right)^2$$

$$K_{C2} = \frac{103943}{\exp\left[\frac{-9834}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right]}$$

$$k_{f,1} = 0.933\exp\left[2.5\left(\frac{31400}{R}\left(\frac{1}{330}-\frac{1}{T}\right)\right)\right]\left(\frac{m^3}{mol}\right)^2 s^{-1}$$

$$k_{f,2} = 0.636\exp\left[\frac{18000}{R}\left(\frac{1}{300}-\frac{1}{T}\right)\right]\frac{m^3}{mol\cdot s}$$

$$k_{f,3} = 0.244\exp\left[1.5\left(\frac{28956}{R}\left(\frac{1}{325}-\frac{1}{T}\right)\right)\right]s^{-1}$$

$\Delta H_f^o(CH_3OH) = -201kJ/mol$, $c_{P,CH3OH} = 44J/(mol\cdot K)$

$\Delta H_f^o(CH_2O) = -116kJ/mol$, $c_{P,CH2O} = 35.5J/(mol\cdot K)$

The activation energies in these expression are given in *cal*, and the universal gas constant is R=1.987*cal/mol K*. Assume that the inlet gas and the reactor temperatures are the same.

1. Write down the reaction rate equations for the three reactions.
2. Write down the formation rates for each species in terms of the time rate of change of its molar concentration.
3. Integrate these equations for p = 1, 10 and 100 atm, at temperatures in the given range, take T = 320, 340, 360 and 380 K.
4. Use these results to determine the impact of the pressure on the concentration of methanol in the products. Can you explain this trend form the reaction equations?
5. Use the results to determine the optimum operating conditions for maximizing methanol production in terms of p, T and residence time.
6. How much heat transfer is required in your optimum case to keep the temperature constant within the reactor?

Integrating the differential equations is most easily done using Matlab ordinary differential equations solver, Sungbae will post an example on how to do that.

Problem #2

Consider the electrode reaction O + e = R. Under the conditions that bulk concentrations $[O]*=[R]*=1mM$, $k^o= 10^{-6}cm/s$, and $\alpha=0.3$.

1. Calculate the exchange current density, $j_o=i_o/A$ in microamps/cm^2.
2. Draw a current density – overpotential curve for this reaction for currents up to 600 microamps/cm^2 anodic and cathodic. Neglect mass transfer effects.
3. Draw $\log|j|$ vs. η_a curves for the current ranges in question 2.