Assignment 5 - Solutions

1. Methanol is synthesized in a gas phase reaction

   $CO + 2H_2 \leftrightarrow CH_3OH$

   under *constant pressure* adiabatic PFR. The feed is as per the stoichiometric proportion at 300 K, and C_{A0} = 1 mol/dm^3.

   Standard Gibbs free energy of formation ($g^0_{f,298K}$) and standard enthalpy of formation ($h^0_{f,298K}$) of CO and CH_3OH at 298 K are given in the table below.

Species	$g^0_{f,298K}$ kJ/mol	$h^0_{f,298K}$ kJ/mol
CO	-137.17	-110.53
CH_3OH	-161.96	-200.66

   Assuming heat reaction to be independent of temperature, calculate equilibrium conversion of CO over a temperature range of 300 - 500 K (take an interval of 50 K), and show a rough sketch of the profile. [Note that concentration equilibrium constant (K_C) and true equilibrium constant (K) are related by $K_C C_{A0}^2 = K$, for the above reaction.]

   Solution:

   $g^0_{R,298K} = (g^0_{f,298K})_{CH3OH} - (g^0_{f,298K})_{CO} - 2(g^0_{f,298K})_{H2}$

   $g^0_{R,298K} = -161.96 - (-137.17) - 2(0) = -24.79$ kJ/mol.

   Equilibrium constant: $K(298K) = e^{-\frac{g^0_{R,298K}}{RT}}$

   $$K(298K) = e^{-\frac{-24790}{8.314\times298}} = 22154$$

   Temperature dependence of equilibrium constant

   $$K(T) = K(298K)\, e^{-\frac{h^0_{R,298K}}{R}\left(\frac{1}{298}-\frac{1}{T}\right)}$$

   $h^0_{R,298K} = (h^0_{f,298K})_{CH3OH} - (h^0_{f,298K})_{CO} - 2(h^0_{f,298K})_{H2}$

   $g^0_{R,298K} = -200.66 - (-110.53) - 2(0) = -90.13$ kJ/mol.

   $$K(T) = K(298K)\, e^{\frac{h^0_{R,298K}}{R}\left(\frac{1}{298}-\frac{1}{T}\right)}$$

   $$K(T) = 22154\, e^{\frac{-90130}{8.314}\left(\frac{1}{298}-\frac{1}{T}\right)}$$

   $$K(T) = 22154\, e^{-10841\left(\frac{1}{298}-\frac{1}{T}\right)}$$

T (K)	300	350	400	450	500
K	17383	99.6	2.1	0.1	0.01

Stoichiometry:

Species	**Initial**	**Change**	**final**
CO (A)	F_{A0}	- $F_{A0}X$	F_{A0} (1-X)
H_2 (B)	$F_B = 2F_{A0}$	- $2F_{A0}X$	F_{A0}(2-2X)
CH_3OH (C)	0	$F_{A0}X$	$F_{A0}X$

Concentration: $C_j = C_{A0}\frac{(\Theta_j+\nu_j X)}{(1+\varepsilon X)}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$

$$C_j = C_{A0}\frac{(\Theta_j+\nu_j X)}{(1+\varepsilon X)}\left(\frac{T_0}{T}\right)$$

$$\delta = 1-1-2 = -2$$

$y_{A0} = 1/3$

$$\varepsilon = \delta y_{A0} = -2/3$$

$$C_A = C_{A0}\frac{(1-X)}{\left(1-\frac{2}{3}X\right)}\left(\frac{T_0}{T}\right);\ C_B = C_{A0}\frac{(2-2X)}{\left(1-\frac{2}{3}X\right)}\left(\frac{T_0}{T}\right);\ C_C = C_{A0}\frac{X}{\left(1-\frac{2}{3}X\right)}\left(\frac{T_0}{T}\right)$$

$$-r_A = k_A C_A C_B^2 - k_{-A} C_C$$

$$-r_A = k_A\left(C_A C_B^2 - \frac{C_C}{K_C}\right)$$

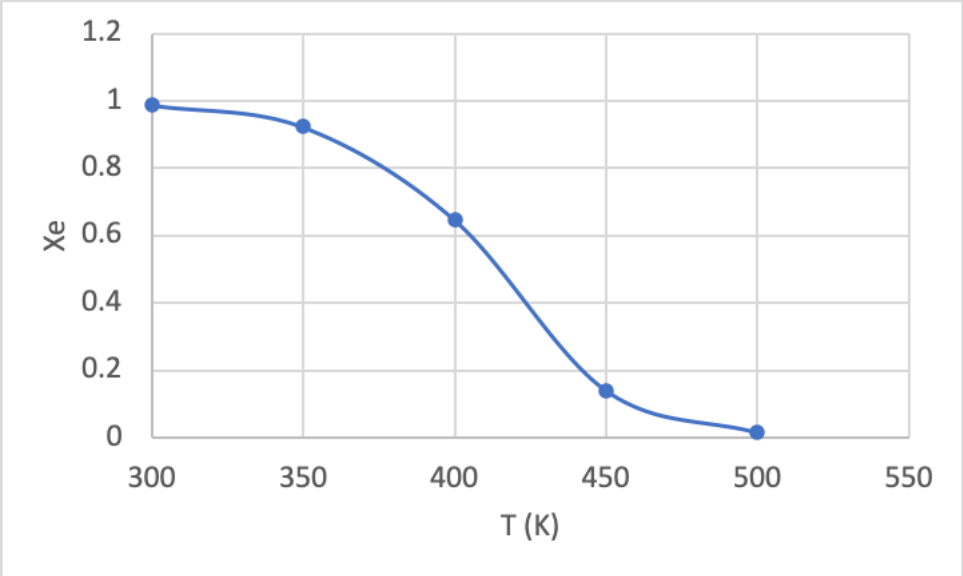
$$= k_A C_{A0}^3\left(4\frac{(1-X)^3}{\left(1-\frac{2}{3}X\right)^3}\left(\frac{T_0}{T}\right)^3 - \frac{X}{K_C C_{A0}^2\left(1-\frac{2}{3}X\right)}\left(\frac{T_0}{T}\right)\right)$$

At equilibrium,

$$K_C C_{A0}^2 = K = \frac{X\left(1-\frac{2}{3}X\right)^2}{4(1-X)^3}\left(\frac{T}{T_0}\right)^2$$

Solve for Xe for a given T and K.

T	300	350	400	450	500
K	17383	99.6	2.1	0.1	0.01
Xe	0.9882	0.923	0.647	0.14	0.015



2. Consider the gas phase pyrolysis of ethane

$C_2H_6 \longleftrightarrow C_2H_4 + H_2$
(A) (C) (D)

Thermodynamic data are given below. Heat capacity as a function of temperature for each species is given by: $\frac{C_{P,i}}{R} = \alpha_i + \beta_i T + \gamma_i T^2$ (T in K)

Species	$h^0_{f,298K}$ kJ/mol	α	β	γ
C_2H_6	-84.68	1.131	19.225×10^{-3}	-5.561×10^{-6}
C_2H_4	52.26	1.424	14.394×10^{-3}	-4.392×10^{-6}
H_2	-	3.249	0.422×10^{-3}	0

Mean heat capacity is defined over a temperature range T_1 to T_2 as:

$$\bar{C}_P = \frac{1}{T_2 - T_1}\int_{T_1}^{T_2} C_P dT$$

Calculate $\bar{C}_P$ over a temperature range of 298 K to 500 K for each species. Using the calculated mean heat capacities, calculate heat of reaction for the above reaction over a temperature range of 298 K - 500K. Based on your result, can you suggest whether or not the heat of reaction can be considered to be independent of temperature over the range 298 - 500?

Solution:

$$\frac{\bar{C}_P}{R} = \alpha + \frac{\beta}{2}(T_2 + T_1) + \frac{\gamma}{3}(T_2 - T_1)^2$$

$$\bar{C}_{P,A} = (1.131 + 7.671 - 0.076)R = 8.726R$$

$$\bar{C}_{P,C} = (1.424 + 5.743 - 0.06)R = 7.11\,R$$

$$\bar{C}_{P,D} = (3.249 + 0.168)R = 3.417\,R$$

$$\Delta C_P = \bar{C}_{P,C} + \bar{C}_{P,D} - \bar{C}_{P,A} = 1.8\,R$$

$$\Delta h_R(T) = \Delta h_R^{\circ}(T_R) + \Delta C_P(T - T_R)$$

$$\Delta h_R^{\circ}(T_R) = \frac{d}{a}h_{f,D} + \frac{c}{a}h_{f,C} - h_{f,A} = h_{f,D} + h_{f,C} - h_{f,A} = 0 + 52.26 - (-84.68)$$

$$\Delta h_R^{\circ}(298\,K) = 137\frac{kJ}{mol}.$$

$$\Delta h_R(T) = 137 + 1.8 \times 8.314 \times 10^{-3} \times (T - 298)$$

$$\Delta h_R(T) = 137 + 0.015 \times (T - 298)\ \text{[kJ/mol]}$$

T (K)	298	350	400	450	500
$\Delta h_R(T)\ kJ/mol$	137	138	13.5	139	140

Yes, heat reaction decreases only by 2% at T = 500K, hence it can be considered constant over 298 - 500 K range.

3. The elementary, irreversible gas-phase reaction

A→B + C

is carried out adiabatically in a PFR packed with a catalyst. Pure A enters the reactor at a volumetric flow rate of 20 dm^3/s, at a pressure of 10 atm, and a temperature of 450 K.

Additional information:
$C_{P,A}$ = 40 J/mol.K, $C_{P,B}$ = 25 J/mol.K , $C_{P,C}$ = 15 J/mol.K

$h_{f,A}^0$ = −70 kJ/mol, $h_{f,B}^0$ = −50 kJ/mol, $h_{f,C}^0$= − 40 kJ/mol. All heats of formation are referenced to 273 K.

$$k = 0.133 \exp\left[\frac{E}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right] \frac{\text{dm}^3}{\text{kg-cat} \cdot \text{s}} \text{ with } E = 31.4 \text{ kJ/mol}$$

Plot the conversion and temperature down the plug-flow reactor until an 80% conversion (if possible) is reached. (The maximum catalyst weight that can be packed into the PFR is 50 kg.) Assume that pressure drop is negligible.

Solution:

PBR performance equation: $\frac{W}{F_{A0}} = \int \frac{dX}{-r_A}$

Rate law: $-r_A = kC_A$ with $k = 0.133e^{\left[\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{T}\right)\right]} \frac{dm^3}{kg-cat.s}$

Stoichiometry: $C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X}$ $\varepsilon = y_{A0}\delta = 1 \times (2-1) = 1$

$$C_A = \frac{C_{A0}(1-X)}{1+X}$$

Energy balance: $T = T_0 - \frac{\Delta h_R^0}{C_{P,A}} X$ as $\Delta C_P = C_{P,B} + C_{P,C} - C_{P,A} = 0$

$$\Delta h_R^0 = h_{f,C}^0 + h_{f,B}^0 - h_{f,A}^0 = -20\ kJ/mol$$

$$T = 450 + 500X$$

Combining: $\frac{W}{F_{A0}} = \int \frac{(1+X)dX}{0.133e^{\left[\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{450+500X}\right)\right]} C_{A0}(1-X)}$

$$\frac{W}{v_0} = \int \frac{(1+X)}{0.133e^{\left[\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{450+500X}\right)\right]}(1-X)} dX$$

The integrant is plotted as a function of X, and it follows a polynomial function given in the figure below.

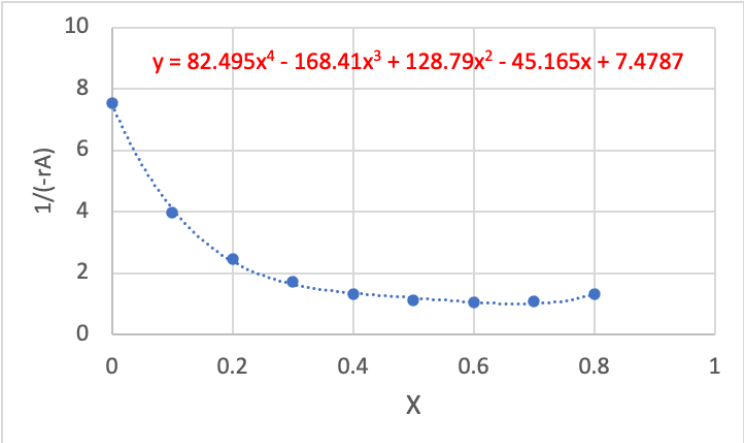


Fig. 1. A plot of $\frac{1}{-r_A}$ vs X.

The function can be analytically integrated for different X values (from 0 to 0.8). The integration value is equal to W/v_0, from which W can be calculated for different X values. Then the plot of X vs W can be made as shown below.

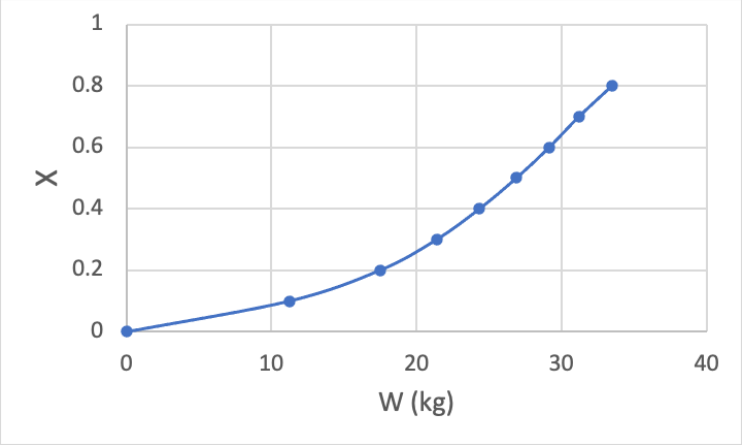


Fig 2. Conversion along the length of the reactor.

Data:

X	T	k	(-rA)	1/(-rA)	W/v0	W
0	450	0.133	0.133	7.51879699	0	0
0.1	500	0.30785522	0.25188154	3.97012024	0.560865	11.2173
0.2	550	0.61174382	0.40782922	2.45200677	0.87372	17.4744
0.3	600	1.08414863	0.58377234	1.71299654	1.069335	21.3867
0.4	650	1.75943947	0.75404549	1.32617994	1.21704	24.3408
0.5	700	2.6645204	0.88817347	1.12590619	1.344525	26.8905
0.6	750	3.81795793	0.95448948	1.04768048	1.45764	29.1528
0.7	800	5.23018097	0.92297311	1.08345518	1.560195	31.2039
0.8	850	6.90433154	0.76714795	1.30352952	1.67376	33.4752