CHEM E 457 Project

Problem 1

Part A.

$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \quad \text{(Reaction 1)}$$

To determine the dissociation energy of a molecule we add up the energy of each of its bonds from Table 2 (D_0 at 298K, units are kJ/mol):

CO_2 :	$C + O \rightarrow CO$	$D_0 = 1076.5$
	$CO + O \rightarrow CO_2$	$D_0 = 532.2$
	Sum the above	+_____
	$C + 2O \rightarrow CO_2$	$D_{0,CO2} = 1608.7$
H_2 :	$H + H \rightarrow H_2$	$D_{0,H2} = 436.0$
CH_3OH :	$C + H \rightarrow CH$	$D_0 = 339.0$
	$CH + H \rightarrow CH_2$	$D_0 = 421.7$
	$CH_2 + H \rightarrow CH_3$	$D_0 = 473.0$
	$O + H \rightarrow OH$	$D_0 = 428.0$
	$CH_3 + OH \rightarrow CH_3OH$	$D_0 = 377.0$
	Sum the above	+_____
	$C + 4H + O \rightarrow CH_3OH$	$D_{0,CH3OH} = 2038.7$
H_2O :	$O + H \rightarrow OH$	$D_0 = 428.0$
	$OH + H \rightarrow H_2O$	$D_0 = 498.7$
	Sum the above	+_____
	$O + 2H \rightarrow H_2O$	$D_{0,H2O} = 926.7$

$$\Delta D_{rxn1} = D_{prod} - D_{react} = D_{0,CH3OH} + D_{0,H2O} - D_{0,CO2} - 3 \times D_{0,H2}$$

$$\Delta D_{rxn1} = 2038.7 + 926.7 - 1608.7 - 3 \times 436.0 = 48.7 \text{ kJ/mol}$$

Part B.

Section I.

Generally:
$$Kp = \frac{p_C^c p_D^d}{p_A^a p_B^b} = (kT)^{c+d-a-b} \frac{q_{C,0}^c q_{D,0}^d}{q_{A,0}^a q_{B,0}^b} e^{\Delta D/RT} \quad \text{(Eqn 1)}$$

Have CO_2 (A), H_2 (B), CH_3OH (C), H_2O (D),

so, a = 1, b = 3, c = 1, d = 1

Now:
$$Kp = \frac{p_{CH3OH} p_{H2O}}{p_{CO2} p_{H2}^3} = (kT)^{-2} \frac{q_{CH3OH,0}^1 q_{H2O,0}^1}{q_{CO2,0}^1 q_{H2,0}^3} e^{\Delta D/RT} \quad \text{(Eqn 2)}$$

We now have to find q_0 for each component:

$$q_0 = \frac{q_{translational}}{V} q_{rotational} q_{vibrational} q_{electric} \quad \text{(Eqn 3)}$$

Translational partition function:

$$\frac{q_{translational}}{V} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \quad \text{(Eqn 4)}$$

where h = 6.63e-34 J·s
k = 1.38e-23 J/K
m = (Mass of molecule in kg)
T = (Temperature in K)
Returns $\frac{q_{translational}}{V}$ in units of m^{-3}

Rotational partition function:

We have some components that have linear rotation and we have some components that have nonlinear rotation, so there must be separate functions in the code for both. CO_2 and H_2 rotate linearly. CH_3OH and H_2O rotate nonlinearly.

Linear:
$$q_{rotational} = \frac{8\pi IkT}{\sigma h^2} \quad \text{(Eqn 5)}$$

Nonlinear:
$$q_{rotational} = \frac{(\pi I)^{\frac{1}{2}}}{\sigma} \left(\frac{8*pi*k*T}{h^2}\right)^{\frac{3}{2}} \quad \text{(Eqn 6)}$$

where h = 6.63e-34 J·s
k = 1.38e-23 J/K
I = (Moment of inertia. Approximately 1D for linear rotation
and 3D for nonlinear rotation. Given in Table 1.)
σ = (Symmetry factor. Given in Table 1.)
T = (Temperature in K)

Returns $q_{rotational}$ as a unitless number

Vibrational partition function:

We are given $\theta_{vibration}$ for all components, so we can use the following equation to find $q_{vibrational}$:

$$q_{vibrational} = \frac{1}{1-e^{\theta vibration/T}} \quad \text{(Eqn 7)}$$

where $\theta_{vibration}$ = (Vibrational temperature in K. Given in Table 1)
        T = (Temperature in K)
    Returns $q_{vibrational}$ as a unitless number

Electric partition function:

$\theta_{electronic}$ is large and T is relatively small for all components, so $q_{electronic} = g_0$. $g_0 = 1$ for all of our components (Table 1), so,

$$q_{electronic} = 1 \quad \text{(Eqn 8)}$$

We can now substitute Equations 4, 5, 6, 7, and 8 into Equation 3 to get q_0 for each component. Then we can solve Equation 2. For this equation we want to use k with different units than above so that the final units of K_p are atm^{-2}.

$$Kp = (kT)^{-2} \frac{q_{CH3OH,0} q_{H2O,0}}{q_{CO2,0} q_{H2,0}^3} e^{\Delta D/RT} \quad \text{(Eqn 2)}$$

where k = 1.36267e-28 m^3 atm K^{-1}
        R = 0.00184 kJ/mol
        ΔD_{rxn1} = 48.7 kJ/mol
        T = (Temperature in K)

Section II.

Plot of K_p for T varying from 50 to 1500 degrees Celsius is attached (Figure 1).

Section III.

The van't Hoff relation is:

$$\frac{\partial \ln K_p}{\partial(^1/_T)} = -\frac{\Delta H^\circ}{R} \quad \text{(Eqn 9)}$$

Solving for ΔH°:

$$\Delta H^\circ = -R \frac{\partial \ln K_p}{\partial(^1/_T)} \quad \text{(Eqn 10)}$$

where R = 0.00184 kJ/mol

Attached (Figure 2) is a plot of $\frac{\ln K_p}{(^1/_T)}$. The slope of Figure 2 is $\frac{\partial \ln K_p}{\partial(^1/_T)}$. Two points were chosen near the center of the figure.

$$\frac{\partial \ln K_p}{\partial(^1/_T)} = \frac{-11.36961-(-12.80985)}{0.001216545- 0.001084599} = 10915.34$$

$$\Delta H_1^\circ = -0.00184 \frac{kJ}{mol} 10915.34 = -88.8 \text{ kJ/mol}$$

Section IV.

$\Delta H°$ from heats of formation ($\Delta H_f°$) is equal to the heats of formation of the products minus the heats of formation of the reactants:

$\Delta H_{rxn1} = \Delta H_{prod} - \Delta H_{react} = \Delta H_{0,CH3OH} + \Delta H_{0,H2O} - \Delta H_{0,CO2} - 3 \times \Delta H_{0,H2}$

Heats of formation are given in Table 1

$\Delta H_{0,CH3OH} = -201.0 \text{ kJ/mol}$

$\Delta H_{0,H2O} = -241.8 \text{ kJ/mol}$

$\Delta H_{0,CO2} = -393.5 \text{ kJ/mol}$

$\Delta H_{0,H2} = 0 \text{ kJ/mol}$

$\Delta H_{rxn1} = (-201.0) + (-241.8) - (-393.5) = -49.3 \text{ kJ/mol}$

This value is 39.5 kJ/mol different from the value from the van't Hoff relation. This could be different because of which points were chosen when the van't Hoff plot was analyzed as well as differences in the change in enthalpy from temperature changes.

Part C.

$$CO_2 + H_2 \leftrightarrows CO + H_2O \quad \text{(Reaction 2)}$$

Section I.

To determine dissociation energy, we once again add up the energy of each of the bonds in the molecule. We already have $D_{0,CO2}$, $D_{0,H2}$, and $D_{0,H2O}$ from part A:

$$D_{0,CO2} = 1608.7, \qquad D_{0,H2} = 436.0, \qquad D_{0,H2O} = 926.7$$

$D_{0,CO}$ is provided in Table 2:

CO: $\qquad$ $C + O \rightarrow CO$ $\qquad\qquad$ $D_{0,CO} = 1076.5$

$\Delta D_{rxn2} = D_{prod} - D_{react} = D_{0,CO} + D_{0,H2O} - D_{0,CO2} - D_{0,H2}$

$\Delta D_{rxn2} = 1076.5 + 926.7 - 1608.7 - 436.0 = -41.5 \text{ kJ/mol}$

Section II.

Using the same procedure as part B, section I:

$$Kp = \frac{p_{CO}p_{H2O}}{p_{CO2}p_{H2}} = (kT)^0 \frac{q^1_{CH3OH,0}q^1_{H2O,0}}{q^1_{CO2,0}q^1_{H2,0}} e^{\Delta D/RT} \qquad \text{(Eqn 10)}$$

The properties of CO are given as well and can be plugged into the same partition function equations as in Part B, Section I.

Section III.

Plot of K_p for T varying from 50 to 1500 degrees Celsius is attached (Figure 3)

Section IV.

Attached (Figure 4) is a plot of $\frac{\ln K_p}{(1/T)}$. We can once again use Equation 10 to find $\Delta H°$. The slope of Figure 4 is $\frac{\partial \ln K_p}{\partial (1/T)}$. Two points were chosen near the center of the figure.

$$\frac{\partial \ln K_p}{\partial (1/T)} = \frac{-1.835137 - (3.386798)}{0.001607717 - 0.0007032349} = -5773.397$$

$$\Delta H_1° = -0.00184 \frac{\text{kJ}}{\text{mol}} (-5773.397) = 47.0 \text{ kJ/mol}$$

Section V.

Same procedure as Part D, Section IV:

$\Delta H_{rxn2} = \Delta H_{prod} - \Delta H_{react} = \Delta H_{0,CO} + \Delta H_{0,H2O} - \Delta H_{0,CO2} - \Delta H_{0,H2}$

Heats of formation are given in Table 1

$\Delta H_{0,CO} = -110.5 \text{ kJ/mol}$

$\Delta H_{0,H2O} = -241.8 \text{ kJ/mol}$

$\Delta H_{0,CO2} = -393.5 \text{ kJ/mol}$

$\Delta H_{0,H2} = 0$ kJ/mol

$\Delta H_{rxn1} = (-110.5) + (-241.8) - (-393.5) = 41.2$ kJ/mol

This value is 6.8 kJ/mol less than the value from the van't Hoff relation. They agree fairly well but may vary slightly because of the temperature dependence of the change in enthalpy.

Section VI.

Attached are plots for $\Delta H°$ (Figure 5), $\Delta \mu°$ (Figure 6), and $\Delta S°$ (Figure 7).

All three plots are approximately linear. Both the change in enthalpy and the change in entropy increase with temperature while the change in chemical potential decreases with temperature. The enthalpy change represents the expansion of the gasses in the reactor as temperature increases. The entropy change represents the increased movement of the particles as temperature increases, which raises the overall entropy. The change chemical potential represents the energy level of the reactants compared to the products. Since the products are entropically favored, as temperature increases, the chemical potential becomes negative.

Section VII.

Reaction two reaches equilibrium when $\Delta \mu°$ for the reaction is equal to zero. From Figure 6, we can see that this occurs at 510 °C.

Part D.

Section I.

A plot of K_{p1}' from 100°C to 400°C is attached (Figure 8).

Section II.

A plot of K_1' from 100°C to 400°C is attached (Figure 9).

Section III.

In both plots, we can see that equilibrium is affected by pressure differently at different temperatures. From 100°C to 200°C, raising the pressure pushes equilibrium toward the products (CH_3OH and H_2O). From 200°C to 400°C, raising the pressure instead pushes equilibrium toward the reactants (CO_2 and H_2).

Section IV.

$$\frac{\partial \ln K_p}{\partial(p)} = -\frac{\Delta v°}{kT} \qquad \text{(Eqn 11)}$$

A plot of $\ln K_p$ vs pressure at 100°C is attached (Figure 10). From this plot we can see that the slope $\frac{\partial \ln K_p}{\partial(p)}$ between 10 atm and 100 atm is linear. Using this slope, we can solve for $\Delta v°$.

$$\frac{\partial \ln K_p}{\partial(p)} = \frac{35.19609 - 33.09722}{100 - 10} = 0.02332$$

$$\Delta v° = kT\frac{\partial \ln K_p}{\partial(p)} = 0.08205 \cdot 373K \cdot 0.02332 = 0.7137 \text{ L/mol}$$

Section V.

Three strategies to increase the methanol production are:

- Increase the amount of hydrogen in the feed. The hydrogen partial pressure dominates the expression for Kp, so a higher fraction of hydrogen will push the reaction more toward the products.
- Keep the temperature below 150 degrees Celsius. Past this temperature the CO2 conversion gets generally worse.
- Keep the pressure above 10 atm. Below 10 atm the CO2 conversion gets much worse.

The most optimal and realistic set of conditions for this reactor are near 125 degrees Celsius and 10 atm. At these conditions the equilibrium constant is high and remains steady for a moderate range of temperatures and pressures which allows for some error when realistically running the reactor.