Gannon Short

CHEM E 457

CHEM E 457 Project

Problem 1

Part A.

CO2 + 3H2 ⇆ CH3OH + H2O (Reaction 1)

To determine the dissociation energy of a molecule we add up the energy of each of its bonds from Table 2 (D0 at 298K, units are kJ/mol):

CO2 : C + O → CO D0 = 1076.5

CO + O → CO2 D0 = 532.2

Sum the above +\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

C + 2O → CO2 D0,CO2 = 1608.7

H2 : H + H → H2 D0,H2 = 436.0

CH3OH : C + H → CH D0 = 339.0

CH + H → CH2 D0 = 421.7

CH2 + H → CH3 D0 = 473.0

O + H → OH D0 = 428.0

CH3 + OH → CH3OH D0 = 377.0

Sum the above +\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

C + 4H + O → CH3OH D0,CH3OH = 2038.7

H2O : O + H → OH D0 = 428.0

OH + H → H2O D0 = 498.7

Sum the above +\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

O + 2H → H2O D0,H2O = 926.7

ΔDrxn1 = Dprod  – Dreact = D0,CH3OH + D0,H2O – D0,CO2 – 3 × D0,H2

ΔDrxn1 = 2038.7 + 926.7 – 1608.7 – 3 × 436.0 = 48.7 kJ/mol

Part B.

Section I.

Generally: (Eqn 1)

Have CO2 (A), H2 (B), CH3OH (C), H2O (D),

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

Now: (Eqn 2)

We now have to find *q0* for each component:

(Eqn 3)

Translational partition function:

(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 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. CO2 and H2 rotate linearly. CH3OH and H2O rotate nonlinearly.

Linear: (Eqn 5)

Nonlinear: (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 as a unitless number

Vibrational partition function:

We are given θvibration for all components, so we can use the following equation to find *qvibrational* :

(Eqn 7)

where = (Vibrational temperature in K. Given in Table 1)

T = (Temperature in K)

Returns as a unitless number

Electric partition function:

θelectronic is large and T is relatively small for all components, so .

for all of our components (Table 1), so,

(Eqn 8)

We can now substitute Equations 4, 5, 6, 7, and 8 into Equation 3 to get *q0* 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 Kp are atm-2.

(Eqn 2)

where k = 1.36267e-28 m3 atm K-1

R = 0.00184 kJ/mol

ΔDrxn1 = 48.7 kJ/mol

T = (Temperature in K)

Section II.

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

Section III.

The van’t Hoff relation is:

(Eqn 9)

Solving for :

(Eqn 10)

where R = 0.00184 kJ/mol

Attached (Figure 2) is a plot of . The slope of Figure 2 is . Two points were chosen near the center of the figure.

Section IV.

from heats of formation () is equal to the heats of formation of the products minus the heats of formation of the reactants:

ΔHrxn1 = ΔHprod  – ΔHreact = ΔH0,CH3OH + ΔH0,H2O – ΔH0,CO2 – 3 × ΔH0,H2

Heats of formation are given in Table 1

ΔH0,CH3OH = –201.0 kJ/mol

ΔH0,H2O = –241.8 kJ/mol

ΔH0,CO2 = –393.5 kJ/mol

ΔH0,H2 = 0 kJ/mol

ΔHrxn1 = (–201.0) + (–241.8) – (–393.5) = –49.3 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.

CO2 + H2 ⇆ CO + H2O (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 D0,CO2, D0,H2, and D0,H2O from part A:

D0,CO2 = 1608.7, D0,H2 = 436.0, D0,H2O = 926.7

D0,CO is provided in Table 2:

CO: C + O → CO D0,CO = 1076.5

ΔDrxn2 = Dprod  – Dreact = D0,CO + D0,H2O – D0,CO2 – D0,H2

ΔDrxn2 = 1076.5 + 926.7 – 1608.7 – 436.0 = –41.5 kJ/mol

Section II.

Using the same procedure as part B, section I:

(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 Kp for T varying from 50 to 1500 degrees Celsius is attached (Figure 3)

Section IV.

Attached (Figure 4) is a plot of . We can once again use Equation 10 to find . The slope of Figure 4 is . Two points were chosen near the center of the figure.

Section V.

Same procedure as Part D, Section IV:

ΔHrxn2 = ΔHprod  – ΔHreact = ΔH0,CO + ΔH0,H2O – ΔH0,CO2 – ΔH0,H2

Heats of formation are given in Table 1

ΔH0,CO = –110.5 kJ/mol

ΔH0,H2O = –241.8 kJ/mol

ΔH0,CO2 = –393.5 kJ/mol

ΔH0,H2 = 0 kJ/mol

ΔHrxn1 = (–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 (Figure 5), (Figure 6), and (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 for the reaction is equal to zero. From Figure 6, we can see that this occurs at 510 .

Part D.

Section I.

A plot of from 100 to 400 is attached (Figure 8).

Section II.

A plot of from 100 to 400 is attached (Figure 9).

Section III.

In both plots, we can see that equilibrium is affected by pressure differently at different temperatures. From 100 to 200, raising the pressure pushes equilibrium toward the products (CH3OH and H2O). From 200 to 400, raising the pressure instead pushes equilibrium toward the reactants (CO2 and H2).

Section IV.

(Eqn 11)

A plot of vs pressure at 100 is attached (Figure 10). From this plot we can see that the slope between 10 atm and 100 atm is linear. Using this slope, we can solve for .

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.