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ChemE 457 Project

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1. The dissociation energy of each of the molecules can be determined by adding up the dissociation of the bonds until all of the bonds between atoms are broken for a single molecule. Assume that the temperature is 298K.

**CO2:**

(1) CO2 🡪 CO + O = 532.2 kJ/mol

(2) CO 🡪 C + O = 1076.5 kJ/mol

Dissociation energy CO2 = (1) + (2) = 1608.7 kJ/mol

**H2:**

Dissociation energy H2 = 436.0 kJ/mol

**CH3OH:**

1. CH3OH 🡪 CH3 + OH = 377.0 kJ/mol
2. OH 🡪 O + H = 428.0 kJ/mol
3. CH3 🡪 CH2 + H = 473.0 kJ/mol
4. CH2 🡪 CH + H = 421.7 kJ/mol
5. CH 🡪 C + H = 339.0 kJ/mol

Dissociation energy CH3OH = (1) + (2) + (3) + (4) + (5) = 2038.7 kJ/mol

**H2O:**

1. H2O 🡪 H + OH = 498.7 kJ/mol
2. OH 🡪 O + H = 428.0 kJ/mol

Dissociating energy H2O = (1) + (2) = 926.7 kJ/mol

CO2 + 3H2 🡪 CH3OH + H2O

* To find the change in dissociation energy of the reaction you add the dissociation energies of the products and subtract the dissociation energies of the reactants

DD = - 1608.7 - 3(436.0) + 2038.7 + 926.7

DD = 48.7 kJ/mol

1. i)

Kp = (kT)(1+1-1-3)(qCH3OHqH2O)/(qCO2qH23)eDD/RT

(kT)-2 = (1.38E-23J/K)-2 \* T-2

(kT)-2 = 5.251E45 T-2 [J-2]

eDD/RT = e(48700J/mol)/(8.314J/mol/K \* T)

eDD/RT = e(5857.6/T)

q = qtrans\*qrot\*qvib\*qelec

* g0 can be used to model qelec because q is much greater than T; g0 = 1

qCH3OH = (2pmCH3OHk/h2)3/2VT3/2 \* (p(IaIbIc)1/2/ s)(8p2k/h2)3/2T3/2 \* (1/(1-e- qCH3OH /T)) \* g0

qCH3OH = (2p(0.03204/6.02E23)k/h2)3/2VT3/2 \* (p(7.894E-117 \* 1E-21)1/2/1)(8p2k/h2)3/2T3/2 \* (1/(1-e-2128/T))

= 3.408E28(T3/2) \* 1.091 (T3/2) \* (1/(1-e-2128/T) \* V

= 3.72E28 (T3) (1/(1-e-2128/T) V

qH2O = (2pmH2OkT/h2)3/2V \* (p(IaIbIc)1/2/ s)(8p2kT/h2) \* (1/(1-e-qH2O/T)) \* g0

qH2O = (2p(0.01802/6.02E23)k/h2)3/2VT3/2 \* (p(5.84\*E-120 \* 1E-21)1/2/2)(8p2k/h2)T \* (1/(1-e-2375/T))

= 1.437E28 (T3/2) \* 0.0297 (T3/2) \* (1/(1-e-2375/T)) \* V

= 4.27E26 (T3) (1/(1-e-2375/T) V

qH2 = (2pmH2kT/h2)3/2V \* (8pIH2kT/ s h2) \* (1/(1-e-qH2/T)) \* g0

qH2 = (2p(0.00202/6.02E23)k/h2)3/2(T3/2) \* (8p(4.6E-41 \* 1E-7)k/ 2h2) (T) \* (1/(1-e-6339/T))\*V

= 5.394E26 (T3/2) \* 1.817E-3(T) \*(1/(1-e-6339/T)) \* V

= 9.8E23 T5/2 \*(1/(1-e-6339/T)) V

qCO2 = (2pmCO2kT/h2)3/2V \* (8pICO2kT/ s h2) \* (1/(1-e-qCO2/T)) \* V

= (2p(0.04401/6.02E23)k/h2)3/2(T3/2) \* (8p(7.174E-39 \* 1E-7)k/ 2h2) (T) \* (1/(1-e-3451/T)) \* V

= 5.486E28 (T3/2) \* 0.283 (T) \* (1/(1-e-3451/T)) \* V

= 1.55E28 (T5/2) \* (1/(1-e-3451/T)) \* V

Set V = 1 m3 (Assumed Reactor Size)

(qCH3OHqH2O)/(qCO2qH23) = [(3.72E28 (T3) (1/(1-e-2128/T)) \* 4.27E26 (T3) (1/(1-e-2375/T)] / [(9.8E23 T5/2 \*(1/(1-e-6339/T)))^3 \* (1.55E28 (T5/2) \* (1/(1-e-3451/T)))]

Kp = 5.251E45 T-2 \* [(3.72E28 (T3) (1/(1-e-2128/T)) \* 4.27E26 (T3) (1/(1-e-2375/T)] / [(9.8E23 T5/2 \*(1/(1-e-6339/T)))^3 \* (1.55E28 (T5/2)) \* (1/(1-e-3451/T)))] \* e(5857.6/T)

ii)

See attached graph 1

iii)

ln(Kp) = ln(5.251E45 T-2) + ln(3.72E28 (T3)) + ln((1/(1-e-2128/T)) + ln(4.27E26 (T3)) + ln(1/(1-e-2375/T)) - ln((9.8E23 (T5/2))^3) - ln((1/(1-e-6339/T))^3) - ln(1.55E28 (T5/2))

- ln(1/(1-e-3451/T)) + 5857.6/T

See attached graph 2: ln(Kp) vs 1/T

-DH/R = slope = (-19.2646 + 21.0125)/(0.00309454 – 0.00287233)

-DH/R = 7866.0

DH = -65400 J/mol = -65.4 kJ/mol

iv)

DHf(CH3OH) = -201.0 kJ/mol

DHf(H2O) = -241.8 kJ/mol

DHf(CO2) = -393.5 kJ/mol

DHf(H2) = 0 kJ/mol

DHreaction = (-201.0) + (-241.8) – (-393.5) – 3(0)

DHreaction = -49.3 kJ/mol

The calculated value from Van’t Hoff’s equation and from the heats of formation are comparable but not super close to each other. They both predict the exothermic nature of the reaction and they are both in the same order of magnitude. The % error of the Van’t Hoff value isn’t more than 200%. The line on the Van’t Hoff graph also isn’t perfectly linear which could further affect the accuracy of the calculation. The values taken for slope were the 2 rightmost points on the graph.

1. i)

CO2 + H2 🡪 CO + H2O

CO 🡪 C + O = 1076.5 kJ/mol

Dissociation energy CO = 1076.5 kJ/mol

DD = -1608.7 - 436.0 + 1076.5 + 926.7

DD = - 41.5 kJ/mol

ii)

Kp = (kT)(1+1-1-1)(qCOqH2O)/(qCO2qH2)eDD/RT

(kT)1+1-1-1 = (kT)0 = 1

eDD/RT = = e(-41500J/mol)/(8.314J/mol/K \* T)

eDD/RT = e(-4991.6/T)

q = qtrans\*qrot\*qvib\*qelec

* g0 can be used to model qelec because q is much greater than T; g0 = 1

qCO = (2pmCOkT/h2)3/2V \* (8pICOkT/ s h2) \* (1/(1-e-qCO/T)) \* V

= (2p(0.02801/6.02E23)k/h2)3/2(T3/2) \* (8p(1.449E-39 \* 1E-7)k/ 1h2) (T) \* (1/(1-e-3126/T)) \* V

= 2.786E28 (T3/2) \* 0.1145 (T) \* (1/(1-e-3126/T)) \* V

= 3.190E27 (T5/2) \* (1/(1-e-3126/T)) \* V

qH2O = (2pmH2OkT/h2)3/2V \* (p(IaIbIc)1/2/ s)(8p2kT/h2) \* (1/(1-e-qH2O/T)) \* g0

= 4.27E26 (T3) (1/(1-e-2375/T) V (From part b)

qCO2 = (2pmCO2kT/h2)3/2V \* (8pICO2kT/ s h2) \* (1/(1-e-qCO2/T)) \* V

= 1.55E28 (T5/2) \* (1/(1-e-3451/T)) \* V (From part b)

qH2 = (2pmH2kT/h2)3/2V \* (8pIH2kT/ s h2) \* (1/(1-e-qH2/T)) \* g0

= 9.8E23 T5/2 \*(1/(1-e-6339/T)) V (From part b)

Set V = 1 m3 (Assumed Reactor Size)

(qCOqH2O)/(qCO2qH2) = [3.190E27 (T5/2) \* (1/(1-e-3126/T)) \* 4.27E26 (T3) (1/(1-e-2375/T)] / [9.8E23 T5/2 \*(1/(1-e-6339/T)) \* (1.55E28 (T5/2) \* (1/(1-e-3451/T)))]

Kp = [3.190E27 (T5/2) \* (1/(1-e-3126/T)) \* 4.27E26 (T3) (1/(1-e-2375/T)] / [9.8E23 T5/2 \*(1/(1-e-6339/T)) \* (1.55E28 (T5/2) \* (1/(1-e-3451/T)))] \* e(-4991.6/T)

iii)

See attached graph 3

iv)

ln(Kp) = ln(3.190E27 (T3)) + ln((1/(1-e-3126/T)) + ln(4.27E26 (T3)) + ln(1/(1-e-2375/T)) - ln((9.8E23 (T5/2))) - ln((1/(1-e-6339/T))) - ln(1.55E28 (T5/2)) - ln(1/(1-e-3451/T)) – 4991.6/T

See attached graph 4: ln(Kp) vs 1/T

-DH/R = slope = (-8.0608 + 6.914)/( 0.00309454 – 0.00287233)

-DH/R = -5160.9

DH = 42900 J/mol = 42.9 kJ/mol

v)

DHf(CO) = -110.5 kJ/mol

DHf(H2O) = -241.8 kJ/mol

DHf(CO2) = -393.5 kJ/mol

DHf(H2) = 0 kJ/mol

DHreaction = (-110.5) + (-241.8) – (-393.5) – (0)

DHreaction = 41.2 kJ/mol

The answer calculated from Van’t Hoff’s equation from Kp is very similar to that calcualted from the heats of formation from each molecule in the reaction. The slight differences could be from the assumption that DH is constant with respect to T meaning that the Van’t Hoff graph is perfectly linear over the range of T values.

vi)

Dh = slope of the tangent of the Van’t Hoff graph \* (-R)

This was done by finding the slope of a theoretical line drawn from the current point and the point that follows

See attached graph 5: enthalpy of reaction 2 as a function of T

Dh remains fairly constant with temperature. The graph increases a little bit over the temperature range because it is such a wide range of temperatures so change in properties is to be expected. It is mostly linear. It represents the energy required to react 1 mole of reactants.

ln(Kp) = -Dm/RT

Dm = -RTln(Kp)

See attached graph 6: chemical potential of reaction 2 as a function of T

Dm begins out positive at lower temperatures in the range, then around 400 degrees Celsius it crosses the x-axis and becomes negative. It is mostly linear. The chemical potential represents the change in free energy with respect to the change in one of its components.

Dm = Dh – TDs

Ds = (Dh – Dm)/T

See attached graph 7: entropy of reaction 2 as a function of T

The entropy graph increases over a small range and is always greater than 0 with a slight downwards concavity decreasing its slope. The entropy represents the possible states that a system could be in or also defined as the “chaos” of a system

vii)

See attached graph 6 and graph 8: Kp vs reverse reaction Kp

The reaction is at equilibrium when the change in chemical potential of the reaction is equal to zero and when the forward and reverse Kp is equal to each other. This occurs at 370 degrees Celsius or 643 K

1. i)

CO2 + 3H2 🡪 CH3OH + H2O

Kp’ = (PCH3OHPH2O)/(PCO2PH23)

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nCO2 = (1- conversion%)

nH2 = (3\*nCO2)

nCH3OH = (conversion %)

nH2O = (conversion %)

P0 = Feed pressure

P = P0 \* (new moles / old moles)

P = P0 \* (nCO2+nH2+nCH3OH+nH2O)/4

PCO2 = P \* (nCO2/(nCO2 + nH2 + nCH3OH + nH2O))

PH2 = P \* (nH2/(nCO2 + nH2 + nCH3OH + nH2O))

PCH3OH = P \* (nCH3OH/(nCO2 + nH2 + nCH3OH + nH2O))

PH2O = = P \* (nH2O/(nCO2 + nH2 + nCH3OH + nH2O))

See attached graph 9: Kp1’ at different pressures

ii)

K’ = (NCH3OHNH2O)/(NCO2NH23)

RT = (P + a(N/V)2)(V/N – b)

Use rootfinder to find N for each molecule

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Description automatically generated

V = 1 L

R = 0.08206 (L atm/ mol K)

P = Partial pressure of that species at that temperature and volume

nCO2 = (1- conversion%)

nH2 = (3\*nCO2)

nCH3OH = (conversion %)

nH2O = (conversion %)

P0 = Feed pressure

P = P0 \* (new moles / old moles)

P = P0 \* (nCO2+nH2+nCH3OH+nH2O)/4

PCO2 = P \* (nCO2/(nCO2 + nH2 + nCH3OH + nH2O))

PH2 = P \* (nH2/(nCO2 + nH2 + nCH3OH + nH2O))

PCH3OH = P \* (nCH3OH/(nCO2 + nH2 + nCH3OH + nH2O))

PH2O = = P \* (nH2O/(nCO2 + nH2 + nCH3OH + nH2O))

See attached graph 10: K1’ at different pressures

iii)

At lower temperatures, pressure has a very dramatic effect on the equilibrium of the reaction. At high pressure and low temperature, the conversion of CO2 was much greater than at low pressure and low temperature. When you look at the higher temperature ranges, the pressure still has a big effect, but not as much as it did at lower temperature. In this temperature range higher pressure still converted more CO2 than lower pressure and thus pushing equilibrium towards the products more than lower pressure did. Higher pressures consistently pushed equilibrium towards the products side more than the lower pressures did but having a greater impact at lower temperature.

iv)

dln(K)/dP = -Dv/kT

see attached graph 11: lnK1’ vs P at 100 degrees C

slope = (34.41 – 22.93)/(100 – 10) atm^-1 \* (1atm/101325Pa) = 1.259E-6 pa^-1

1.259E-6 = -Dv/kT; T = 373 K, R = 8.314 J/molK

Dv = -(1.259E-6)(373)(8.314)

Dv = -0.0039 m^3/mol

v)

The first strategy to improving the effectiveness of this reactor is to run it at a lower temperature. Based on the temperature ranges given you’d want the temperature of your reactor closer to 100 degrees Celsius. The first desired reaction is exothermic, and the second undesired reaction is endothermic, which means that adding heat will result in undesired products. As a result of this we get the best conversion in to CH3OH at lower temperatures.

A second strategy that would improve the effectiveness of the reactor is to run it at high pressure. Combined with lower temperature, this would further push the reaction equilibrium towards the products side of reaction 1 giving us more desired product. The greatest conversion is given when P = 100 atm however this is not practical considering you can get almost as much from a reactor feed pressurized to 10 atm. Because there is such a drop off when temperature increases at 10 atm I would recommend running the reactor at around 15 or 20 atm.

Thirdly, because under the above recommendations the rate constant is so high it means that more feed (3 H2: 1 CO2 ratio) can be given to the reactor without much consequence because the feed will react quickly. You’ll want to stay at a 3:1 feed ratio because the reaction can only consume 3 moles H2 for 1 mole CO2. By doing this, you will still be able to have an efficient reactor.