Chemical Engineering Thermodynamics

Quiz 14

April 25, 2019

Glycerol is a byproduct of biodiesel production as a result of trans-esterification of methanol. This glycerol is normally refined to 99.9 wt% and then sold for use in cosmetics and food. However, this is fairly costly and usually results in a loss. It is desirable to convert glycerol to a new product that would be of either higher value or of more use to the production facility. One proposed solution is to use steam reforming to produce a combination of natural gas (CH_4) and syn-gas (CO and H_2). The natural gas can then be used to offset the energy requirements of the production facility, and the synthesis gas can be used to make methanol. The process of steam reforming involves three coupled reactions:

$$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 3CO_2(g) + 7H_2(g) \tag{1}$$

$$2C_3H_8O_3(g) + H_2(g) \leftrightarrow 3CH_4(g) + 3CO(g) + 3H_2O(g) \tag{2}$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \tag{3}$$

	Thermochemical Data		Heat Capacity Constants (J/mol)			
Component	ΔH_f^0(298K) (KJ/mol)	ΔG_f^0(298K) (KJ/mol)	a	b	c	d
$C_3H_8O_3$ (Glycerol)	-579	-465	8.4	0.44	-3.2e-04	9.4e-08
H_2O (Water)	-242	-229	32.2	1.9e-03	1.1e-05	-3.6e-09
CO_2 (Carbon Dioxide)	-394	-394	19.8	73.4e-03	-5.6e-05	1.7e-08
H_2 (Hydrogen)	0	0	27.1	9.3e-03	-1.4e-05	7.6e-09
CH_4 (Methane)	-75	-50	19.3	52.1e-03	1.2e-05	-1.1e-08
CO (Carbon Monoxide)	-111	-137	30.9	-12.9e-03	2.8e-05	-1.3e-08

a) Use the Kcal.xls spreadsheet to calculate the K_a for each of these three reactions at **750K. USE THE THERMOCHEMICAL DATA GIVEN ABOVE.**

b) **Calculate the enthalpy of reaction for each of the reactions.** Are the reactions **endothermic or exothermic**?

c) Make a table for reaction (1) alone based on stoichiometry to **calculate the mole fractions** of each component at thermodynamic equilibrium. Assume 1 mole of glycerol and 5 moles of steam as the feed. **Give the limits for the reaction coordinate, ξ_1.**

d) Write an expression for the equilibrium constant for reaction (1) based on the mole fractions and the pressure.

e) Use Solver® to find the extent of reaction of reaction, ξ_1 (1). ***P* = 2000 bar; *T* = 750K.**

f) Make a table to calculate **the mole fractions** for all 3 reactions run together. Assume a feed of 1 mole of glycerol, 1 mole of carbon monoxide, and 5 moles of steam. **Give the limits for the three reaction coordinates, ξ_1, ξ_2, and ξ_3.**

g) Write expressions for the 3 equilibrium constants for the three reactions based on the mole fractions and the pressure.

Answer Sheet **NAME: ______________________________**

a) K_{a1} =

K_{a2} =

K_{a3} =

b) ΔH_1 = Reaction 1 endo or exothermic:

ΔH_2 = Reaction 2 endo or exothermic:

ΔH_3 = Reaction 3 endo or exothermic:

c)

Component	**Initial (n_i)**	**Final (n_f)**	y_i
Total			

LIMITS for ξ_1:

d) K_{a1} =

e) ξ_1 =

f)

Component	**Initial (n_i)**	**Final (n_f)**	y_i
Total			

LIMITS for ξ_1:

LIMITS for ξ_2:

LIMITS for ξ_3:

g) $K_{a1} =$

$K_{a2} =$

$K_{a3} =$

Answer Sheet **NAME:** ______________________________

a) $K_{a1} =$ 4.03e19

$K_{a2} =$ 3.30 e42

$K_{a3} =$ 4.87

b) $\Delta H_1 =$ 155 kJ/mol Reaction 1 endo or exothermic: endothermic

$\Delta H_2 =$ −131 kJ/mol Reaction 2 endo or exothermic: exothermic

$\Delta H_3 =$ −37.3 Reaction 3 endo or exothermic: exo

c)

Component	Initial (n_i)	Final (n_f)	y_i
$C_3H_8O_3$	1	$1-\xi$	$\frac{1-\xi}{6+6\xi}$
H_2O	5	$5-3\xi$	$\frac{5-3\xi}{6+6\xi}$
CO_2	0	3ξ	$\frac{3\xi}{6+6\xi}$
H_2	0	7ξ	$\frac{7\xi}{6(1+\xi)}$
Total	6	$6+6\xi$	1

LIMITS for ξ_1: $0 \le \xi \le 1$

d) $K_{a1} = \dfrac{P^6}{(6+6\xi)^6} \dfrac{(3\xi)^3(7\xi)^7}{(1-\xi)(5-3\xi)^3}$

e) $\xi_1 =$ 0.823

f)

Component	Initial (n_i)	Final (n_f)	y_i
$C_3H_8O_3$	1	$1-\xi_1-2\xi_2$	
H_2O	5	$5-3\xi_1+3\xi_2-\xi_3$	
CO_2	0	$3\xi_1+\xi_3$	
H_2	0	$7\xi_1-\xi_2+\xi_3$	
CH_4	0	$3\xi_2$	
CO	1	$1+3\xi_2-\xi_3$	
Total	7	$7+6\xi_1+6\xi_2$	

✓

LIMITS for ξ_1: $-\frac{1}{3} \le \xi_1 \le 1$

LIMITS for ξ_2: $0 \le \xi_2 \le \frac{1}{2}$

LIMITS for ξ_3: $-3 \le \xi_3 \le \frac{3}{2}$

by looking at the reactions & the feed amounts

g) $K_{a1} = \dfrac{P^6}{(7+6\xi_1+6\xi_2)^6} \dfrac{(3\xi_1+\xi_3)^3(7\xi_1-\xi_2+\xi_3)^7}{(1-\xi_1-2\xi_2)(5-3\xi_1+3\xi_2-\xi_3)^3}$

$K_{a2} = \dfrac{P^6}{(7+6\xi_1+6\xi_2)^6} \dfrac{(3\xi_2)^3(1+3\xi_2-\xi_3)^3(5-3\xi_1+3\xi_2-\xi_3)^3}{(1-\xi_1-2\xi_2)^2(7\xi_1-\xi_2+\xi_3)}$

$K_{a3} = \dfrac{(3\xi_1+\xi_3)(7\xi_1-\xi_2+\xi_3)}{(5-3\xi_1+3\xi_2-\xi_3)(1+3\xi_2-\xi_3)}$