**Chemical Engineering Thermodynamics**
**Quiz 14**
**April 20, 2017**

The Sabatier reaction (eqn. 17.31) is used to produce methane from hydrogen for introduction into existing natural gas distribution systems. For example excess solar or wind power could be used to perform electrolysis of water and the $H_2$ converted to methane by this reaction. It might be possible to couple the water gas shift reaction (eqn. 17.32) to enhance conversion of $H_2$ to $CH_4$ since the water-gas shift reaction both consumes the byproduct of the Sabatier reaction and produces the two reactants. Calculate the conversion of $CO_2$ in the absence of the water-gas shift reaction and in its presence at 625°K and 2 bar.

$$CO_{2(g)} + 4H_{2(g)} \rightleftarrows CH_{4(g)} + 2H_2O_{(g)} \qquad \text{Sabatier} \qquad 17.31$$

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)} \qquad \text{Water-gas shift} \qquad 17.32$$

| | $\Delta H_f$ (298°K) | $\Delta G_f$ (298°K) | $\nu_1$ | $\nu_2$ |
|---|---|---|---|---|
| | kJ/mol | kJ/mol | | |
| CO | -111 | -137 | 0 | -1 |
| $H_2O$ | -242 | -229 | 2 | -1 |
| $CO_2$ | -394 | -394 | -1 | 1 |
| $H_2$ | 0 | 0 | -4 | 1 |
| $CH_4$ | -74.9 | -50.5 | 1 | 0 |

a) Use Kcal.xls to calculate $K_a$ for the two reactions **at 625°K**. (***Copy the heat capacity values from the PREOS.xls "ig CPs" sheet, CO is carbon monoxide, $CH_4$ is methane.)***
b) Make a table for the Sabatier reaction run alone based on the stoichiometry to calculate the mole fractions. **Use 1 mole $CO_2$, 4 moles of $H_2$ as feed**.
c) Write an expression for the equilibrium constants based on the mole fractions and pressure (2 bar) for the Sabatier alone.
d) Use Excel to write a spreadsheet and use solver to find the conversion of the Sabatier reaction alone (reaction coordinate for reaction 1). Make sure to include limits on the reaction coordinate (you have one mole of $CO_2$ initially and no moles of $CH_4$ initially).
e) Make a table for the two reactions run together **adding 2 moles of CO per mole of $CO_2$** that is added (do not add water).
f) Write an expression for the two equilibrium constants based on the mole fractions and pressure (2 bar) for the Sabatier in combination with the water-gas shift reaction.
g) Use Excel to write a spreadsheet to solve for the conversions of the two reactions. Make sure to include limits on the two reaction coordinates (you have the possibility of three moles of $CO_2$ if rxn 2 goes to completion and no moles of $CH_4$ initially; you have two moles of CO initially and one mole of $CO_2$).
h) Make an assessment of using the water-gas shift reaction to enhance the Sabatier reaction conversion. Calculate moles $CH_4$ produced to moles $CO_2$ added as a measure of the efficiency.

Answer Quiz 14
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a) $K_{a_1} = 25,900$

$K_{a_2} = 16.5$

b)

| | | $n_i$ | $n_f$ | $y_i$ |
|---|---|---|---|---|
| 1 | $CO_2$ | 1 | $1-\xi_1$ | $(1-\xi_1)/(5+\xi_1)$ |
| 2 | $H_2$ | 4 | $4(1-\xi_1)$ | $4(1-\xi_1)/(5+\xi_1)$ |
| 3 | $CH_4$ | 0 | $\xi_1$ | $\xi_1/(5+\xi_1)$ |
| 4 | $H_2O$ | 0 | $2\xi_1$ | $2\xi_1/(5+\xi_1)$ |
| | | sum $5+\xi_1$ | | |

c) $$K_{a_1} = \frac{\xi_1 (2\xi_1)^2 (5+\xi_1)^2}{(1-\xi_1)\, 4^4 (1-\xi_1)^4 P^2}$$

$$= \frac{4\xi_1^3 (5+\xi_1)^2}{4^3 4 (1-\xi_1)^5 P^2} = \frac{\xi_1^3 (5+\xi_1)^2}{64 (1-\xi_1)^5 P^2}$$

d) $\xi_1 = 0.916$ $\quad 0 \le \xi_1 \le 1$

e)

| | | $n_i$ | $n_f$ | $Y_i$ |
|---|---|---|---|---|
| 1 | $CO_2$ | 1 | $1-\xi_1+\xi_2$ | $(1-\xi_1+\xi_2)/(7-2\xi_1)$ |
| 2 | $H_2$ | 4 | $4-4\xi_1+\xi_2$ | $(4(1-\xi_1)+\xi_2)/(7-2\xi_1)$ |
| 3 | $CH_4$ | 0 | $\xi_1$ | $\xi_1/(7-2\xi_1)$ |
| 4 | $H_2O$ | 0 | $2\xi_1-\xi_2$ | $(2\xi_1-\xi_2)/(7-2\xi_1)$ |
| 5 | $CO$ | 2 | $2-\xi_2$ | $(2-\xi_2)/(7-2\xi_1)$ |
| | | | $7-2\xi_1$ | |

f)

$$K_{a_1} = \frac{\xi_1 (2\xi_1-\xi_2)^2 (7-2\xi_1)^2}{(1-\xi_1+\xi_2)(4(1-\xi_1)+\xi_2)^4 P^2}$$

$$K_{a_2} = \frac{(4(1-\xi_1)+\xi_2)(1-\xi_1+\xi_2)}{(2-\xi_2)(2\xi_1-\xi_2)}$$

g)

$0 \le \xi_1 \le 3$ $\qquad \xi_1 = 1.53$

$-1 \le \xi_2 \le 2$ $\qquad \xi_2 = 2$

Rxn 2 runs to completion

h) For the Sabatier alone

$$\frac{n_{CO_4}}{n_{CO_2 \text{ added}}} = \frac{\xi_1}{1} = 0.916$$

For the dual reaction scheme

$$\frac{n_{CH_4}}{n_{CO_2\ added}} = \frac{\xi_1}{1} = 1.53$$

On the other hand

$$\frac{n_{CH_4\ produced}}{n_{CO_2\ added} + n_{CO\ added}} = \frac{1.53}{3} = 0.51$$

The efficiency depends on how you define the problem