Exercise 13

1. Reaction Equilibrium

Determine the expressions for the two equilibrium constants of the system characterized by the two chemical reactions:

CH4 + H2O = CO + 3H2

CH4 + 2H2O = CO2 + 4H2

Assume ideal gas.

Let rx 1: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

rx2: $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$

And the extent of each reaction be ξ_1 for rx1 and ξ_2 for rx 2.

The reactions are linearily independent, so we already have linearily independent system.

We did the same problem in the lectures, and used $n_{CH_4,0} = 1$ and $n_{H_2O,0} = 2$, so I will do the same for simplicity

Component	CH_4	H_2O	CO	CO_2	H_2
V_1	-1	-1	1	0	3
V_2	-1	-2	0	1	4
n_{i0}	1	2	0	0	0
n_i	$1-\xi_1-\xi_2$	$2-\xi_1-2\xi_2$	ξ_1	ξ_2	$3\xi_1+4\xi_2$

We have that the total number of moles in the system is given by: $n = \Sigma n_i = (1-\xi_1-\xi_2) + (2-\xi_1-2\xi_2) + \xi_1 + \xi_2 + (3\xi_1+4\xi_2)$

$$n = 3 + 2\xi_1 + 2\xi_2$$

Using that $y_i = \frac{n_i}{n}$, we get:

$$y_{CH_4} = \frac{1-\xi_1-\xi_2}{3+2\xi_1+2\xi_2}$$

$$y_{H_2O} = \frac{2-\xi_1-2\xi_2}{3+2\xi_1+2\xi_2}$$

$$y_{CO} = \frac{\xi_1}{3+2\xi_1+2\xi_2}$$

$$y_{CO_2} = \frac{\xi_2}{3+2\xi_1+2\xi_2}$$

$$y_{H_2} = \frac{3\xi_1+4\xi_2}{3+2\xi_1+2\xi_2}$$

In the lectures, it was shown that for the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

by assuming ideal gas, the equilibrium constant is given by:

$$K \overset{ig}{=} \frac{y_C^c \cdot y_D^d}{y_A^a \cdot y_B^b} \cdot \left(\frac{P}{P^\circ}\right)^{c+d-a-b}$$

Applying this to the two reactions, the equilibrium constants can be found:

$$K_1 = \frac{y_{CO} \cdot y_{H_2}^3}{y_{CH_4} \cdot y_{H_2O}} \cdot \left(\frac{P}{P_\circ}\right)^{1+3-1-1}$$

$$K_2 = \frac{y_{CO_2} \cdot y_{H_2}^4}{y_{CH_4} \cdot y_{H_2O}^2} \cdot \left(\frac{P}{P^\circ}\right)^{1+4-1-2}$$

$$K_1 = \frac{\dfrac{\xi_1}{(3+2\xi_1+2\xi_2)} \cdot \dfrac{(3\xi_1+4\xi_2)^3}{(3+2\xi_1+2\xi_2)^3}}{\dfrac{(1-\xi_1-\xi_2)}{(3+2\xi_1+2\xi_2)} \cdot \dfrac{(2-\xi_1-2\xi_2)}{(3+2\xi_1+2\xi_2)}} \cdot \left(\frac{P}{P^\circ}\right)^2$$

$$K_2 = \frac{\dfrac{\xi_2}{(3+2\xi_1+2\xi_2)} \cdot \dfrac{(3\xi_1+4\xi_2)^4}{(3+2\xi_1+2\xi_2)^4}}{\dfrac{(1-\xi_1-\xi_2)}{(3+2\xi_1+2\xi_2)} \cdot \dfrac{(2-\xi_1-2\xi_2)^2}{(3+2\xi_1+2\xi_2)^2}} \cdot \left(\frac{P}{P^\circ}\right)^2$$

$$K_1 = \frac{\xi_1(3\xi_1+4\xi_2)^3}{(1-\xi_1-\xi_2)(2-\xi_1-2\xi_2)(3+2\xi_1+2\xi_2)^2} \cdot \left(\frac{P}{P^\circ}\right)^2$$

$$K_2 = \frac{\xi_2(3\xi_1+4\xi_2)^4}{(1-\xi_1-\xi_2)(2-\xi_1-2\xi_2)^2(3+2\xi_1+2\xi_2)^2} \cdot \left(\frac{P}{P^\circ}\right)^2$$