## Exercise 1

CH4 (g) is used as a source to generate hydrogen for a vehicle fuel cell. Methane and water vapor are introduced into a reforming plant. This plant converts these two streams into $CO_2$, CO and $H_2$, having also $H_2O$ in the outlet stream of the reformer.

Considering that the reactor is fed with 1.125 kg $H_2O$/kg $CH_4$, the output temperature of the products being 750 K and the operating pressure of 1 atm.
a) Determine the molar composition of the products.
b) What happens if we increase the temperature to 850K?
c) What happens if we increase the pressure to 500 kPa?

Gasification is an incomplete combustion of the fuel. In a fuel-rich combustion, the intermediate species such as CO becomes a major product species. If water is added to the reaction, hydrogen is also produced. Because both CO and $H_2$ can be burnt later with oxygen and can release heat, the gasification has been used to convert low-grade fuels, such as, coal and biomass, to a higher grade gaseous fuel, CO and $H_2$.

The reforming chemical reaction for steam:

$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO$

The equilibrium constant is given as a function of the molar fractions or numbers of moles of the substances involved, dependent on the temperature in degrees Kelvin.

$$K_{SR} = \frac{y_{H2}^3 y_{CO}}{y_{CH4} y_{H2O}} P_{TOT}^2 = \frac{n_{H2}^3 n_{CO}}{n_{CH4} n_{H2O} n_{TOT}^2} P_{TOT}^2 = \exp(30.42 - 27106/T) \qquad (1)$$

In the reformer, the "water gas shift" reaction is:

$CO + H_2O \leftrightarrow H_2 + CO_2$

The equilibrium constant is given as a function of the molar fractions or numbers of moles of the substances involved, dependent on the temperature in degrees Kelvin.

$$K_{WGS} = \frac{y_{H2} y_{CO2}}{y_{CO} y_{H2O}} = \frac{n_{H2} n_{CO2}}{n_{CO} n_{H2O}} = \exp(-3.798 + 4160/T) \qquad (2)$$

The resulting gases are: methane ($CH_4$), carbon monoxide (CO), water ($H_2O$), carbon dioxide ($CO_2$), and hydrogen ($H_2$).

Assuming that we start with one mole of methane and one mole of water, and no other chemical compounds, and define $x_1$ as the steam reforming reaction conversion and $x_2$ as the water-gas shift reaction conversion, the following information is available on each of the chemicals in the reactor:

| Formula | Initial (mol) | Change (mol) | End (mol) |
|---|---|---|---|

| | | | |
|---|---|---|---|
| $CH_4$ | 1 | $-x_1$ | $1-x_1$ |
| $H_2O$ | 1 | $-x_1-x_2$ | $1-x_1-x_2$ |
| $CO_2$ | 0 | $x_2$ | $x_2$ |
| CO | 0 | $x_1-x_2$ | $x_1-x_2$ |
| $H_2$ | 0 | $3x_1+x_2$ | $3x_1+x_2$ |
| Total moles | 2 | $2x_1$ | $2+2x_1$ |

Since the total pressure is 1 atm:

$$K_{SR} = \frac{(3x_1 + x_2)^3 (x_1 - x_2)}{(1 - x_1)(1 - x_1 - x_2)(2 + 2x_1)^2} = \exp(30.42 - 27106/T) \tag{3}$$

$$K_{WGS} = \frac{(3x_1 + x_2)(x_2)}{(x_1 - x_2)(1 - x_1 - x_2)} = \exp(-3.798 + 4160/T) \tag{4}$$

We will use these equations to obtain the equilibrium composition at different temperatures.

## Solution to the problem:

Step 1) Obtaining the equilibrium constants of expressions 3 and 4 at T = 750 K:

$$K_{SR} = \exp(30.42 - 27106/750) = \exp(-5.72) = 0.0033 \tag{5}$$

$$K_{WGS} = \exp(-3.798 + 4160/750) = \exp(1.749) = 5.747 \tag{6}$$

Step 2) Equations 3 and 4 can be solved theoretically, obtaining x1 and x2.

One way to solve this nonlinear system of equations is by using the method of successive substitutions. This method begins by assuming a value of $x_2$ = 0 and solving equation 3 to obtain the value of $x_1$. So, equation 4 is used with the value of x1 to compute the new value of $x_2$. The process is repeated until the values of $x_1$ and $x_2$ do not change.

For example, with $x_2$ = 0, the value of $x_1$ = 0.147. After several iterations, the final results are $x_1$ = 0.183 and $x_2$ = 0.154.

It is important to point out that the initial value of $x_2$ can be different from zero, a value of 0.5 being recommended for very low or very high temperatures.

For high temperatures, $x_1 \sim 1$ and $x_2 \sim 0$. For low temperatures, a good guess is $x_1 \sim x_2$.

The balanced composition:

$n_{CH4} = 1-x_1 = 0.817$
$n_{H2O} = 1-x_1-x_2 = 0.663$
$n_{CO2} = x_2 = 0.154$
$n_{CO} = x_1-x_2 = 0.029$
$n_{H2} = 3x_1+x_2 = 0.703$

Assuming that 1 kmol of $CH_4$ and α kmol of $H_2O$ enter:

$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO$

$CO + H_2O \leftrightarrow H_2 + CO_2$

| Formula | Initial (mol) | Change (mol) | End (mol) |
|---|---|---|---|
| $CH_4$ | 1 | $-x_1$ | $1-x_1$ |
| $H_2O$ | $\alpha$ | $-x_1-x_2$ | $\alpha-x_1-x_2$ |
| $CO_2$ | 0 | $x_2$ | $x_2$ |
| CO | 0 | $x_1-x_2$ | $x_1-x_2$ |
| $H_2$ | 0 | $3x_1+x_2$ | $3x_1+x_2$ |
| Moles totales | $1+\alpha$ | $2x_1$ | $1+\alpha+2x_1$ |

Para una presión diferente a 1 atm:

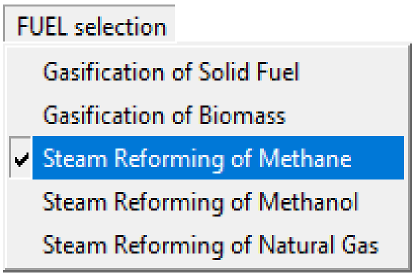
$$K_{SR} = \frac{(3x_1+x_2)^3(x_1-x_2)}{(1-x_1)(\alpha-x_1-x_2)(1+\alpha+2x_1)^2}P_{TOT}^2 = \exp(30.42-27106/T) \qquad (3a)$$

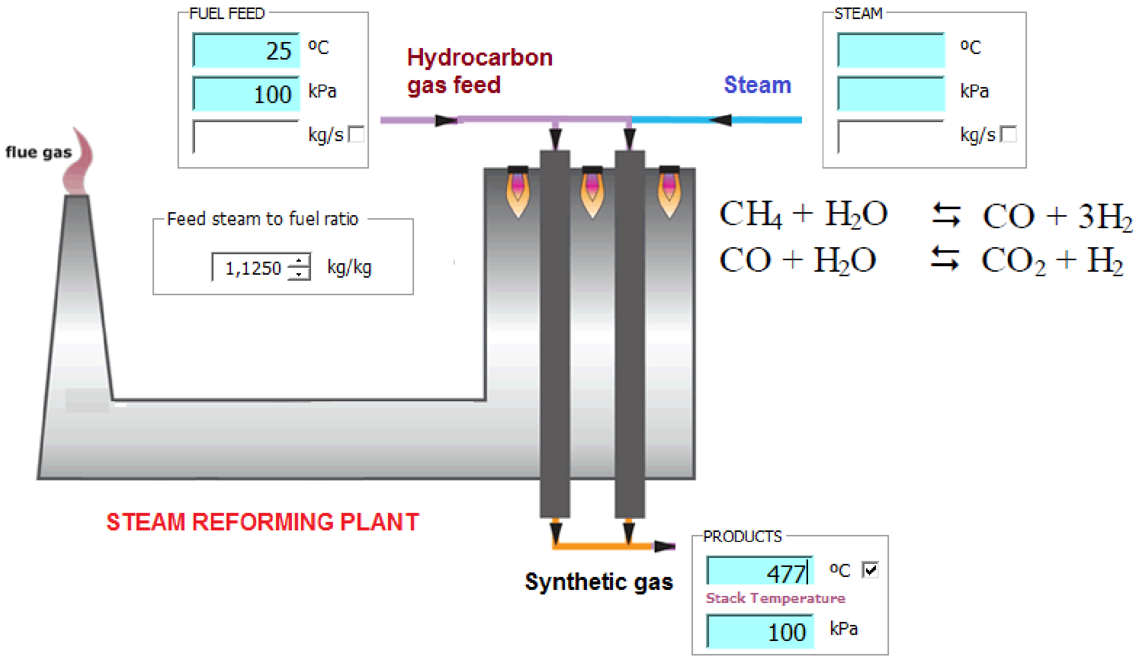
$$K_{WGS} = \frac{(3x_1+x_2)(x_2)}{(x_1-x_2)(\alpha-x_1-x_2)} = \exp(-3.798+4160/T) \qquad (3b)$$

Knowing the number of kilograms of methane and water that enter the reactor, it is very easy to obtain the value of moles of water (α) that enter.

α = kg $H_2O$/ kg $CH_4$ (16/18) kmoles $H_2O$ / kmoles $CH_4$ = 1 kmoles $H_2O$ / kmoles $CH_4$

The "THERMOGasification" software has the calculation algorithms explained in the previous problem. Using it, the following results are achieved:





FUEL FEED

25 ºC

100 kPa

kg/s ☐

STEAM

ºC

kPa

kg/s ☐

Feed steam to fuel ratio

1,1250 kg/kg

PRODUCTS

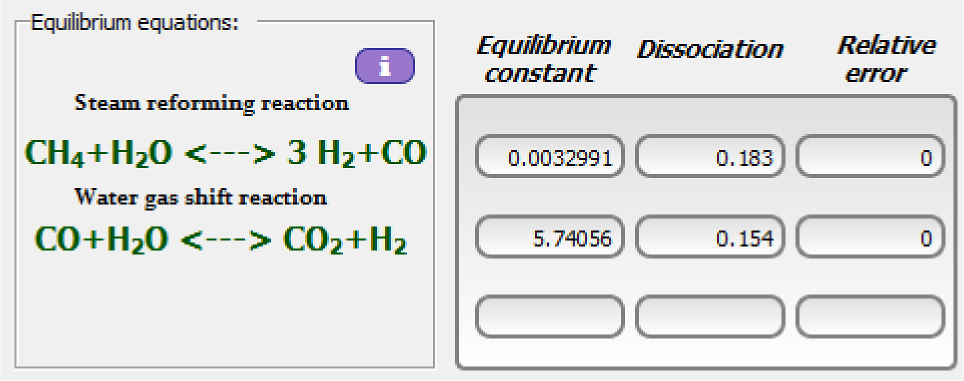
477 ºC ☑

Stack Temperature

100 kPa

$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$

$$CO + H_2O \leftrightarrows CO_2 + H_2$$



Equilibrium equations:

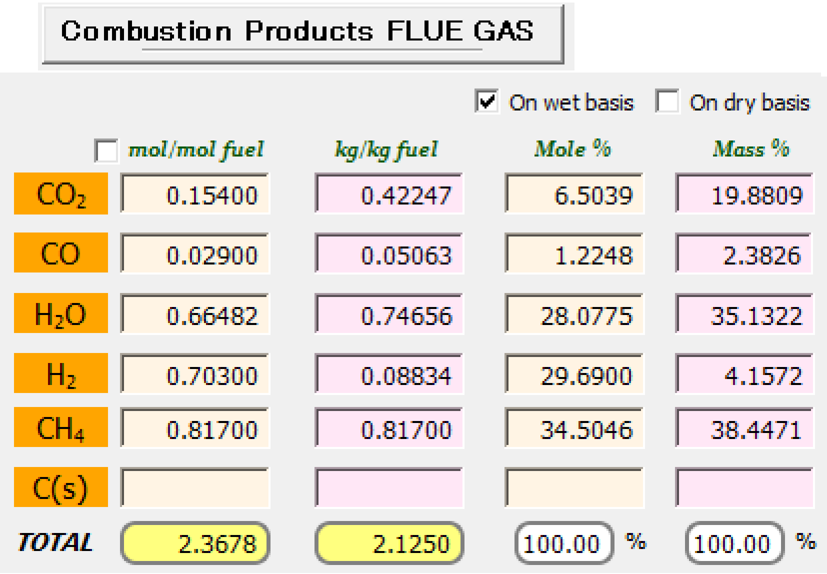
Steam reforming reaction

$CH_4+H_2O$ <---> $3\ H_2+CO$

Water gas shift reaction

$CO+H_2O$ <---> $CO_2+H_2$

| Equilibrium constant | Dissociation | Relative error |
|---|---|---|
| 0.0032991 | 0.183 | 0 |
| 5.74056 | 0.154 | 0 |
| | | |

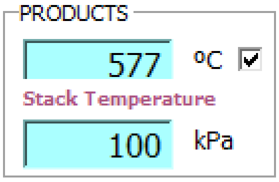


Combustion Products FLUE GAS

☑ On wet basis ☐ On dry basis

| | ☐ mol/mol fuel | kg/kg fuel | Mole % | Mass % |
|---|---|---|---|---|
| $CO_2$ | 0.15400 | 0.42247 | 6.5039 | 19.8809 |
| CO | 0.02900 | 0.05063 | 1.2248 | 2.3826 |
| $H_2O$ | 0.66482 | 0.74656 | 28.0775 | 35.1322 |
| $H_2$ | 0.70300 | 0.08834 | 29.6900 | 4.1572 |
| $CH_4$ | 0.81700 | 0.81700 | 34.5046 | 38.4471 |
| C(s) | | | | |
| TOTAL | 2.3678 | 2.1250 | 100.00 % | 100.00 % |

The results provided by the software are similar to those achieved with the algorithm described above.

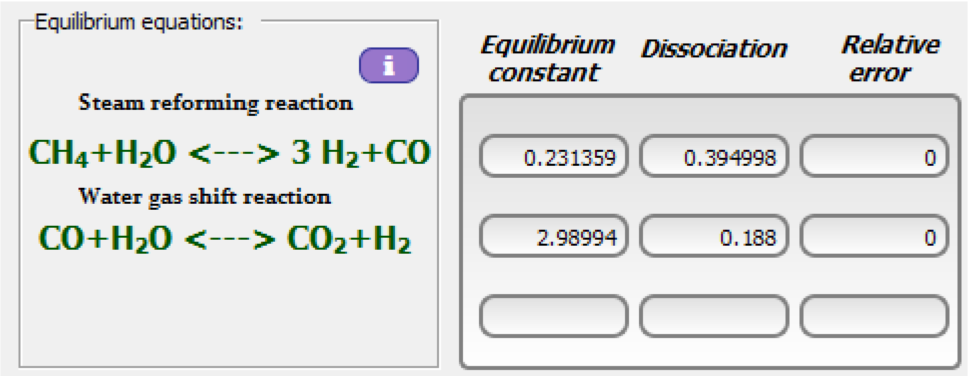


PRODUCTS

577 ºC ☑

Stack Temperature

100 kPa



Equilibrium equations:

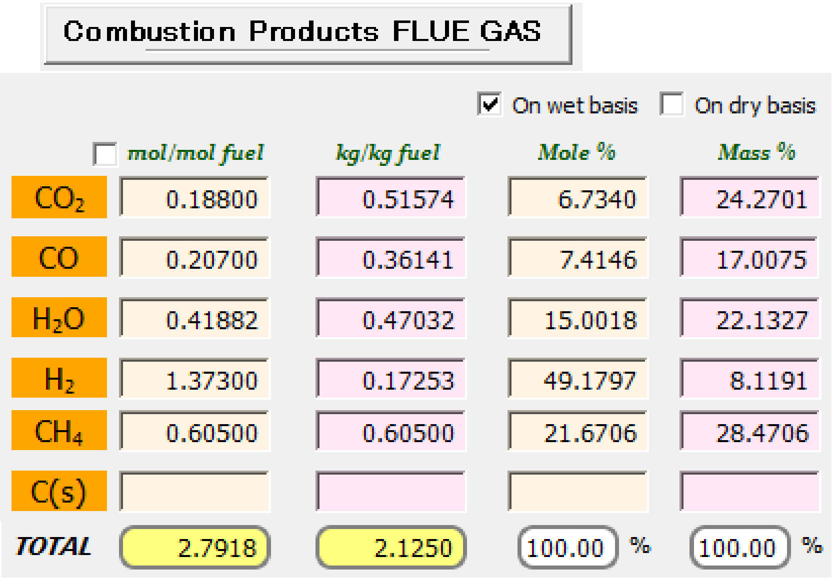
Steam reforming reaction

$CH_4+H_2O <---> 3\ H_2+CO$

Water gas shift reaction

$CO+H_2O <---> CO_2+H_2$

| Equilibrium constant | Dissociation | Relative error |
|---|---|---|
| 0.231359 | 0.394998 | 0 |
| 2.98994 | 0.188 | 0 |
| | | |

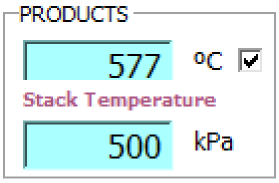


Combustion Products FLUE GAS

☑ On wet basis ☐ On dry basis

| | ☐ mol/mol fuel | kg/kg fuel | Mole % | Mass % |
|---|---|---|---|---|
| $CO_2$ | 0.18800 | 0.51574 | 6.7340 | 24.2701 |
| CO | 0.20700 | 0.36141 | 7.4146 | 17.0075 |
| $H_2O$ | 0.41882 | 0.47032 | 15.0018 | 22.1327 |
| $H_2$ | 1.37300 | 0.17253 | 49.1797 | 8.1191 |
| $CH_4$ | 0.60500 | 0.60500 | 21.6706 | 28.4706 |
| C(s) | | | | |
| *TOTAL* | 2.7918 | 2.1250 | 100.00 % | 100.00 % |

As the temperature increases, the equilibrium constant KSR increases and the constant KWGS decreases, increasing the production of hydrogen and $CO_2$.

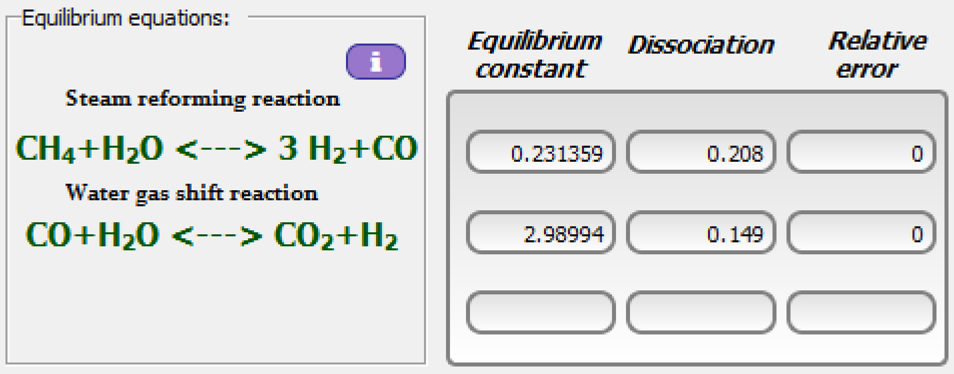


PRODUCTS

577 ºC ☑

Stack Temperature

500 kPa



Equilibrium equations:

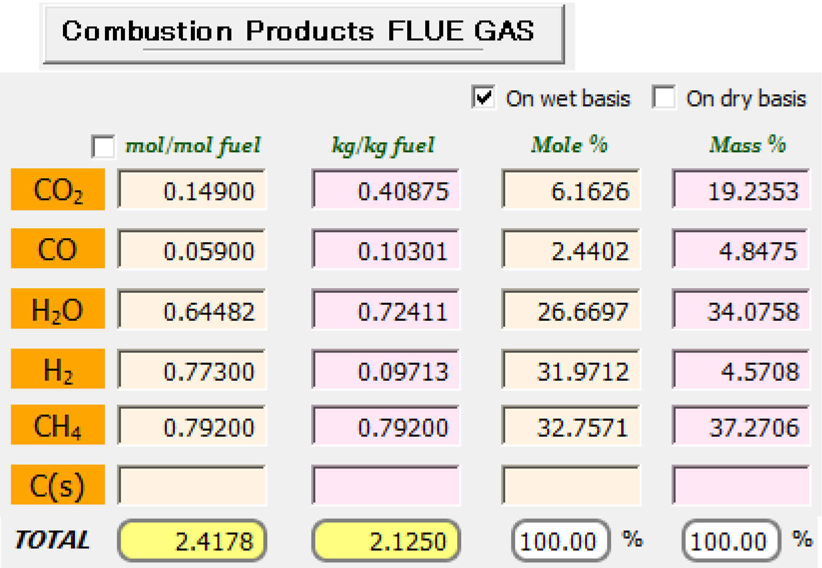
Steam reforming reaction

$CH_4+H_2O$ <---> $3 H_2+CO$

Water gas shift reaction

$CO+H_2O$ <---> $CO_2+H_2$

| Equilibrium constant | Dissociation | Relative error |
|---|---|---|
| 0.231359 | 0.208 | 0 |
| 2.98994 | 0.149 | 0 |
| | | |



Combustion Products FLUE GAS

☑ On wet basis ☐ On dry basis

| | ☐ mol/mol fuel | kg/kg fuel | Mole % | Mass % |
|---|---|---|---|---|
| $CO_2$ | 0.14900 | 0.40875 | 6.1626 | 19.2353 |
| CO | 0.05900 | 0.10301 | 2.4402 | 4.8475 |
| $H_2O$ | 0.64482 | 0.72411 | 26.6697 | 34.0758 |
| $H_2$ | 0.77300 | 0.09713 | 31.9712 | 4.5708 |
| $CH_4$ | 0.79200 | 0.79200 | 32.7571 | 37.2706 |
| C(s) | | | | |
| TOTAL | 2.4178 | 2.1250 | 100.00 % | 100.00 % |

As the pressure increases, the production of hydrogen and $CO_2$ decreases.