



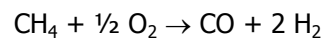
Exercises of "Fundamentals of Chemical Processes"

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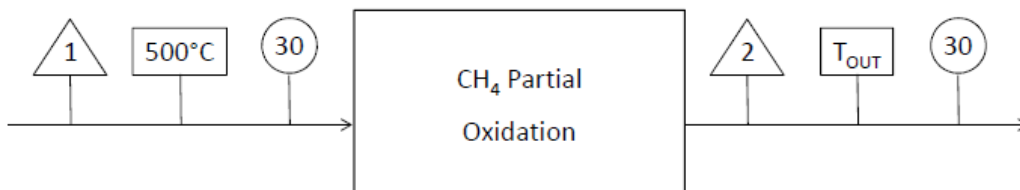
Exercise 6

Estimation of the temperature and the composition at the exit of an adiabatic reactor for the partial oxidation of CH₄

The partial oxidation of CH₄ is carried out in an adiabatic reactor:



Calculate the composition and the temperature of the gas at the exit of the reactor, assuming that equilibrium conditions are reached. CO, H₂, H₂O and CO₂ are present among the products while O₂ is absent.



DATA:

Stream 1: P = 30 atm T = 500°C

Stream 2: P = 30 atm T_{out} = ?

Hypotheses: Thermodynamic equilibrium

Ideal Gas

Adiabatic Reactor

Specie	Flow Rate (Nm ³ /h)
CH ₄	1
O ₂	0.6
H ₂ O	1

ΔG_R^0 is cal/mol, T is K

$$\Delta G_{R,WGS}^0(T) = -8514 + 7.71 \cdot T$$

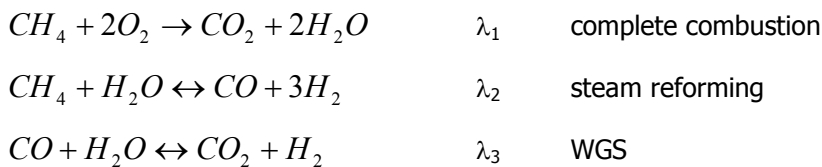
$$\Delta G_{R,SR}^0(T) = +53717 - 60.25 \cdot T$$

Solution

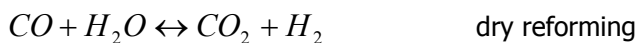
The problem asks for the estimation of the composition and the temperature T_{out} of the gas stream at the exit of the partial oxidation reactor. To solve the problem, the material balances and the enthalpy balance must be coupled, assuming that the reactor is adiabatic and that the gas reaches the thermodynamic equilibrium. 1 mol/h of incoming CH_4 is chosen as the basis for the material balances. Considering the number of the species involved in the process ($NS = 6$) and the number of the atomic species ($NA = 3$), the number of independent reactions that are required to define the solving system are:

$$NR = NS - NA = 6 - 3$$

3 reactions are required to write the material balances. For each of these reactions, it is possible to define an extent of reaction λ_i . The following reactions are chosen:



The choice of the reactions is arbitrary, provided that all the species are involved and that the reactions are linearly independent. For instance, it would have been possible to choose the dry reforming reaction instead of either the steam reforming or the WGS: it is noted indeed that the stoichiometry of the dry reforming reaction is the linear combination of the stoichiometry of the steam reforming and that of the reverse-WGS.



The outlet composition is determined as a function of the extent of the reactions, as follows:

$$n_i^{out} = n_i^{in} + \sum_{j=1}^{NR} \nu_{i,j} \cdot \lambda_j$$

In the equation, j is the number of the reactions involved, i is the number of the species involved and $\nu_{i,j}$ the stoichiometric coefficient of the i -th specie involved in the j -th reaction.

Specie	n^{in} (mol/h)	n^{out} (mol/h)
O₂	0.6	$0.6 - 2\lambda_1$
CH₄	1	$1 - \lambda_1 - \lambda_2$
H₂O	1	$1 + 2\lambda_1 - \lambda_2 - \lambda_3$
CO₂	0	$\lambda_1 + \lambda_3$
H₂	0	$3\lambda_2 + \lambda_3$
CO	0	$\lambda_2 - \lambda_3$
Total	2.6	$2.6 + 2\lambda_2$

The problem of the estimation of the outlet composition is turned into the estimation of 3 unknown values, the extents of the reactions. Taking into account that O₂ is completely consumed and therefore it is absent in the outcoming gas flow, the extent of reaction λ_1 is calculated as follows:

$$2 \cdot \lambda_1 = n_{O_2}^{in} - n_{O_2}^{out} = n_{O_2}^{in} = 0.6 \rightarrow \lambda_1 = 0.3 \text{ mol/h}$$

The thermodynamic equilibrium conditions allow to write two equations, one associated to the steam reforming reaction, and the other to the WGS reaction. Coherently with the assumption of ideal gas, the following equation (Eq. 1) is written for the WGS reaction:

$$k_{eq}^{WGS} = \prod_1^{NC} P_i^{v_i} = \prod_1^{NC} (P \cdot y_i)^{v_i} = \frac{(P \cdot y_{CO_2}^{out}) \cdot (P \cdot y_{H_2}^{out})}{(P \cdot y_{CO}^{out}) \cdot (P \cdot y_{H_2O}^{out})} = \frac{y_{CO_2}^{out} \cdot y_{H_2}^{out}}{y_{CO}^{out} \cdot y_{H_2O}^{out}} = \frac{n_{CO_2}^{out} \cdot n_{H_2}^{out}}{n_{CO}^{out} \cdot n_{H_2O}^{out}} \cdot \frac{n_{tot}^{out} \cdot n_{tot}^{out}}{n_{tot}^{out} \cdot n_{tot}^{out}} =$$

$$= \frac{(\lambda_1 + \lambda_3) \cdot (3\lambda_2 + \lambda_3)}{(\lambda_2 - \lambda_3) \cdot (1 + 2\lambda_1 - \lambda_2 - \lambda_3)}$$

With:

$$k_{eq}^{WGS} = \exp\left(-\frac{-8514 + 7.71 \cdot T_{OUT}}{1.987 \cdot T_{OUT}}\right) = \exp\left(-3.88 + \frac{4284.852}{T_{OUT}}\right)$$

In the case of the steam reforming reaction, the equation (Eq. 2) is:

$$k_{eq}^{SR} = \prod_1^{NC} P_i^{v_i} = \prod_1^{NC} (P \cdot y_i)^{v_i} = \frac{(P \cdot y_{CO}^{out}) \cdot (P \cdot y_{H_2}^{out})^3}{(P \cdot y_{CH_4}^{out}) \cdot (P \cdot y_{H_2O}^{out})} = P^2 \cdot \frac{y_{CO}^{out} \cdot (y_{H_2}^{out})^3}{y_{CH_4}^{out} \cdot y_{H_2O}^{out}} = \frac{P^2}{(n_{tot}^{out})^2} \cdot \frac{n_{CO}^{out} \cdot (n_{H_2}^{out})^3}{n_{CH_4}^{out} \cdot n_{H_2O}^{out}} =$$

$$= \frac{P^2}{(2.6 + 2\lambda_2)^2} \cdot \frac{(\lambda_2 - \lambda_3) \cdot (3\lambda_2 + \lambda_3)^3}{(1 - \lambda_1 - \lambda_2) \cdot (1 + 2\lambda_1 - \lambda_2 - \lambda_3)}$$

with:

$$k_{eq}^{SR} = \exp\left(-\frac{53717 - 60.25 \cdot T_{OUT}}{1.987 \cdot T_{OUT}}\right) = \exp\left(30.322 - \frac{27034.222}{T_{OUT}}\right)$$

The last equation required for the solution of the system is the enthalpy balance on the reactor, given that it is adiabatic.

$$\dot{H}_{IN}(T_{IN}) - \dot{H}_{OUT}(T_{OUT}) = 0$$

Assuming that the reference state is the elementary species at T_{REF} equal to 298K and P_{REF} equal to 1 atm, the molar specific enthalpy for each specie at temperature T is:

$$H_i(T) = \Delta H_{F,i}^0(298K) + \int_{298K}^T C_{p_i} \cdot dT$$

The enthalpy of a gas mixture is calculated as the sum of the product between the specific enthalpy and the molar flow rate of each specie in the mixture.

$$\dot{H}_i(T) = \sum_i^{NC} n_i \cdot H_i(T)$$

The enthalpy balance on the reactor is:

$$\sum_{i=1}^{NC} n_i^{in} \cdot \left(\Delta H_{F,i}^0(298K) + \int_{298K}^{T_{in}} C_{p_i} \cdot dT \right) = \sum_{i=1}^{NC} \left(n_i^{in} + \sum_{j=1}^{NR} \nu_{i,j} \cdot \lambda_j \right) \cdot \left(\Delta H_{F,i}^0(298K) + \int_{298K}^{T_{out}} C_{p_i} \cdot dT \right)$$

$$\sum_{i=1}^{NC} n_i^{in} \cdot \left(a_i \cdot (T_{in} - 298) + \frac{b_i}{2} \cdot (T_{in}^2 - 298^2) + \frac{c_i}{3} \cdot (T_{in}^3 - 298^3) + \frac{d_i}{4} \cdot (T_{in}^4 - 298^4) \right) =$$

$$\sum_{j=1}^{NR} \lambda_j \cdot \left(\Delta H_{R,j}^0(298K) + \Delta a_j \cdot (T_{out} - 298) + \frac{\Delta b_j}{2} \cdot (T_{out}^2 - 298^2) + \frac{\Delta c_j}{3} \cdot (T_{out}^3 - 298^3) + \frac{\Delta d_j}{4} \cdot (T_{out}^4 - 298^4) \right)$$

$$\Delta a_j = \sum_{i=1}^{NC} \nu_{i,j} \cdot a_i$$

Taking the values from the thermodynamic property database (J/mol/K), the following equation is obtained (Eq. 3), which is a function of T_{out} and of the extents of the reaction:

$$\begin{aligned}
& 68.356 \cdot T_{out} + 2.703 \cdot 10^{-2} \cdot T_{out}^2 + 1.100 \cdot 10^{-6} \cdot T_{out}^3 - 5.327 \cdot 10^{-9} \cdot T_{out}^4 + 72166.339 = \\
& -802900 \cdot \lambda_1 + (8.810 \cdot T_{out} + 1.258 \cdot 10^{-2} \cdot T_{out}^2 - 2.727 \cdot 10^{-6} \cdot T_{out}^3 + 1.064 \cdot 10^{-9} \cdot T_{out}^4 - 3105.054) \cdot \lambda_1 + \\
& + 206300 \cdot \lambda_2 + (60.800 \cdot T_{out} - 1.954 \cdot 10^{-2} \cdot T_{out}^2 - 1.202 \cdot 10^{-5} \cdot T_{out}^3 + 6.283 \cdot 10^{-9} \cdot T_{out}^4 - 16114.535) \cdot \lambda_2 + \\
& -41200 \cdot \lambda_3 + (-16.170 \cdot T_{out} + 4.682 \cdot 10^{-2} \cdot T_{out}^2 - 3.609 \cdot 10^{-5} \cdot T_{out}^3 + 1.028 \cdot 10^{-8} \cdot T_{out}^4 + 1534.876) \cdot \lambda_3
\end{aligned}$$

Given that λ_1 is calculated from the specific about O_2 , three unknown values must be determined: λ_2 , λ_3 and T_{out} . The solving system includes the equation derived from the enthalpy balance (Eq. 3) and the two equations derived from the thermodynamic equilibrium, respectively on the steam reforming reaction (Eq. 2) and on the WGS reaction (Eq. 1). The system can be solved following an iterative procedure. For instance, first attempt values are assigned to λ_2 and T_{out} , while λ_3 is derived by solving Equation 2. With this value of λ_3 and with the first attempt value of λ_2 , the outlet temperature T_{out} is derived by solving Equation 3. With the calculated values of λ_3 and T_{out} , λ_2 is calculated from Equation 1, therefore completing the first step of the iterative procedure. The iterative procedure is repeated until the unknown values converge to a stable and physically sound value (6 iteration steps in this case).

Iteration Step	T_{out} [K]	λ_2	λ_3
0	1300.000	0.650	0.100
1	1386.756	0.676	-0.077
2	1355.176	0.693	-0.109
3	1362.204	0.689	-0.102
4	1360.393	0.690	-0.104
5	1360.843	0.690	-0.103
6	1360.730	0.690	-0.103

From the results, it is noted that the extent of the reaction of the WGS is negative. This result indicates that the reverse WGS is active in the reacting system, which consumes CO_2 and H_2 to produce CO and H_2O .