



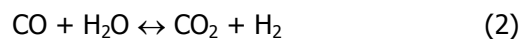
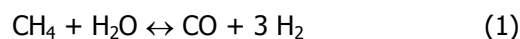
Exercises of “*Fundamentals of Chemical Processes*”

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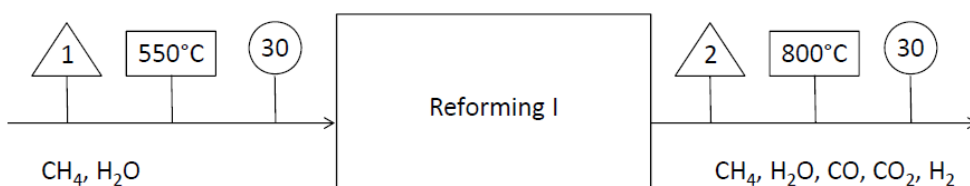
Exercise 5

Estimation of the heat supply Q required by the First Stage of a Reformer

In the first stage of the reforming process, synthesis gas is prepared starting from natural gas. The process can be summarized with the following two reactions:



The second reaction (2) is the Water Gas Shift. The first reaction is the Reforming of methane with steam (steam reforming). This reaction is highly endothermic and the necessary heat is supplied via exchange at the reactor walls. In a typical process, the feed gases (composition given in the Table) enter the reactor at 550°C and exit at 800°C. Assuming that the process reaches the thermodynamic equilibrium, estimate the composition of the outlet gas stream, and find the amount of heat Q to be supplied.



Data:

Stream 1: P = 30 atm T = 550°C

Stream 2: P = 30 atm T = 800°C

Hypothesis: Both the reactions reach the thermodynamic equilibrium
 Ideal mixture of ideal gases

Specie	Flow Rate (Nm ³ /h)
CH ₄	22486
H ₂ O	94015

Solution

The problem asks for the estimation of the heat supply Q and of the composition of the outlet gas stream. For each specie, the material balance is written by applying the extent of reaction method: in this case, two reactions are required, the steam reforming and the WGS. Therefore, it is possible to define the extent of reactions λ_1 and λ_2 . 100 mol/h inlet CH_4 are chosen as the basis for the material balances. The flow rates of the outlet gas stream are expressed as a function of λ_1 and λ_2 :

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

Specie	n^{in} (mol/h)	n^{out} (mol/h)
CH₄	100	$100 - \lambda_1$
H₂O	418.1	$418.1 - \lambda_1 - \lambda_2$
CO	0	$\lambda_1 - \lambda_2$
H₂	0	$3\lambda_1 + \lambda_2$
CO₂	0	λ_2
Total	518.1	$518.1 + 2\lambda_1$

The amount of H_2O in the inlet feed is calculated as follows:

$$H_2O = \frac{94015}{22486} \cdot 100 = 418.1$$

To estimate the extent of the reactions, two equations must be written, knowing that the steam reforming reaction and the WGS reaction reach the thermodynamic equilibrium. The following expressions are given for the estimation of the $\Delta G_R^0(T)$:

$$\Delta G_{R,SR}^0(T) = 53717 - 60.25 \cdot T \quad \text{cal/mol} \quad 600\text{K} < T < 1500\text{K}$$

$$\Delta G_{R,WGS}^0(T) = -8514 + 7.71 \cdot T \quad \text{cal/mol} \quad 600\text{K} < T < 1500\text{K}$$

At T_{OUT} equal to 800°C , the values of the ΔG_R^0 are:

$$\Delta G_{R,SR}^0(1073.15\text{K}) = -10940.29$$

$$\Delta G_{R,WGS}^0(1073.15\text{K}) = -241.2$$

These values lead to:

$$k_{eq}^{SR}(1073K) = 169.12$$

$$k_{eq}^{WGS}(1073K) = 1.12$$



Given the assumption of ideal gases, the equilibrium condition for the steam reforming reaction leads to the following equation (Eq. 1):

$$\begin{aligned} k_{eq}^{SR} &= \prod_1^{NC} P_i^{v_i} = \prod_1^{NC} (P \cdot y_i)^{v_i} = \frac{(P \cdot y_{CO}^{out}) \cdot (P \cdot y_{H_2}^{out})^3}{(P \cdot y_{CH_4}^{out}) \cdot (P \cdot y_{H_2O}^{out})} = P^2 \cdot \frac{y_{CO}^{out} \cdot (y_{H_2}^{out})^3}{y_{CH_4}^{out} \cdot y_{H_2O}^{out}} = P^2 \cdot \frac{n_{CO}^{out} \cdot (n_{H_2}^{out})^3}{n_{CH_4}^{out} \cdot n_{H_2O}^{out}} \cdot \frac{n_{tot}^{out} \cdot (n_{tot}^{out})^3}{n_{tot}^{out} \cdot n_{tot}^{out}} = \\ &= \frac{P^2}{(518.1 + 2\lambda_1)^2} \cdot \frac{(\lambda_1 - \lambda_2) \cdot (3\lambda_1 + \lambda_2)^3}{(100 - \lambda_1) \cdot (418.1 - \lambda_1 - \lambda_2)} \\ &= \frac{900}{(518.1 + 2\lambda_1)^2} \cdot \frac{(\lambda_1 - \lambda_2) \cdot (3\lambda_1 + \lambda_2)^3}{(100 - \lambda_1) \cdot (418.1 - \lambda_1 - \lambda_2)} = 169.12 \end{aligned}$$

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

$$\begin{aligned} k_{eq}^{WGS} &= \prod_1^{NC} P_i^{v_i} = \prod_1^{NC} (P \cdot y_i)^{v_i} = \frac{(P \cdot y_{CO_2}^{out}) \cdot (P \cdot y_{H_2}^{out})}{(P \cdot y_{CO}^{out}) \cdot (P \cdot y_{H_2O}^{out})} = \frac{y_{CO_2}^{out} \cdot y_{H_2}^{out}}{y_{CO}^{out} \cdot y_{H_2O}^{out}} = \frac{n_{CO_2}^{out} \cdot n_{H_2}^{out}}{n_{CO}^{out} \cdot n_{H_2O}^{out}} \cdot \frac{n_{tot}^{out} \cdot n_{tot}^{out}}{n_{tot}^{out} \cdot n_{tot}^{out}} = \\ &= \frac{\lambda_2 \cdot (3\lambda_1 + \lambda_2)}{(\lambda_1 - \lambda_2) \cdot (418.1 - \lambda_1 - \lambda_2)} \\ &= \frac{\lambda_2 \cdot (3\lambda_1 + \lambda_2)}{(\lambda_1 - \lambda_2) \cdot (418.1 - \lambda_1 - \lambda_2)} = 1.12 \end{aligned}$$

Equation 1 and 2 lead to the following solving system:

$$\begin{cases} (\lambda_1 - \lambda_2) \cdot (3\lambda_1 + \lambda_2)^3 = \frac{169.12}{900} \cdot (100 - \lambda_1) \cdot (418.1 - \lambda_1 - \lambda_2) \cdot (518.1 + 2\lambda_1)^2 \\ \lambda_2 \cdot (3\lambda_1 + \lambda_2) = 1.12 \cdot (\lambda_1 - \lambda_2) \cdot (418.1 - \lambda_1 - \lambda_2) \end{cases}$$

Where: $0 < \lambda_1 \leq 100$ and $0 < \lambda_2 \leq \lambda_1$

To solve the system, an iterative procedure can be followed. Different solving strategies are possible. For instance, it is possible to solve Equation 2 as a function of λ_2 , once a value is assigned to λ_1 . A quadratic equation is obtained. The equation has two roots, only one of which has a physical meaning:

$$\lambda_2 = \frac{(3 \cdot \lambda_1 + 468.272) - \sqrt{(-3 \cdot \lambda_1 - 468.272)^2 - 0.48 \cdot (468.272 \cdot \lambda_1 - 1.12 \cdot \lambda_1^2)}}{0.24}$$

A first attempt value is assigned to λ_1 , and λ_2 is determined. With this value of λ_2 , a new value of λ_1 is determined from the first equation. Different numerical methods can be applied in this case, for instance the bisection or the Newton method. With this value of λ_1 , a second new value is obtained for λ_1 . The iterative procedure is repeated until the values converge to stable values. The final solving values are:

$$\lambda_1 = 75.03$$

$$\lambda_2 = 41.88$$

The composition of the outlet gas stream is:

Specie	n^{out} (mol/h)	% dry vol.	% total vol.
CH₄	24.97	6.80	3.74
CO	33.16	9.04	4.96
H₂	266.96	72.75	39.95
CO₂	41.87	11.41	6.27
H₂O	301.20	-	45.08
Total	668.17	100.00	100.00

It is important to note that the partial pressure of the reacting species contemporarily satisfy the equilibrium conditions of both the reactions that are included in the system. It would have been incorrect to solve the equilibrium composition for one reaction, and then determine the equilibrium composition for the other reaction.

The enthalpy balance is used to calculate the heat to be supplied to the reactor:

$$\dot{H}_{IN}(\bar{n}_{IN}, T_{IN}) - \dot{H}_{OUT}(\bar{n}_{OUT}, T_{OUT}) + \dot{Q} = 0$$

The reference state assumes the elementary species at T_{REF} equal to 298.15 K and P_{REF} equal to 1 atm. For each specie in the system, the specific molar enthalpy at temperature T is:

$$H_i(T) = \Delta H_{F,i}^0(298.15K) + \int_{298.15K}^T C_{p,i} \cdot dT$$

The enthalpy of a gas mixture is calculated as the sum of the product between the molar 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 following polynomial form is used for the calculation of the specific heats, taken for the thermodynamic property database:

$$Cp_i(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3$$

$$\int_{298.15K}^T Cp_i dT = \int_{298.15K}^T (a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3) \cdot dT = a_i \cdot (T - 298.15) + \frac{b_i}{2} \cdot (T^2 - 298.15^2) + \frac{c_i}{3} \cdot (T^3 - 298.15^3) + \frac{d_i}{4} \cdot (T^4 - 298.15^4)$$

Knowing the molar flow rates of the gas streams at the inlet and at the outlet of the reactor, the enthalpy of the gas mixtures are calculated once the coefficients for the specific heats are known:

$$\dot{H}_{IN}(\bar{n}_{IN}, T_{IN}) = \sum_{i=1}^{NC} n_i^{in} \cdot \left(a_i \cdot (T_{in} - 298.15) + \frac{b_i}{2} \cdot (T_{in}^2 - 298.15^2) + \frac{c_i}{3} \cdot (T_{in}^3 - 298.15^3) + \frac{d_i}{4} \cdot (T_{in}^4 - 298.15^4) \right)$$

$$\dot{H}_{OUT}(\bar{n}_{OUT}, T_{OUT}) = \sum_{i=1}^{NC} n_i^{out} \cdot \left(a_i \cdot (T_{out} - 298.15) + \frac{b_i}{2} \cdot (T_{out}^2 - 298.15^2) + \frac{c_i}{3} \cdot (T_{out}^3 - 298.15^3) + \frac{d_i}{4} \cdot (T_{out}^4 - 298.15^4) \right)$$

The required values are taken from the thermodynamic property database (J/mol/K):

Specie	$\Delta H^0_F(298K)$ [J/mol]	a	b x 10 ³	c x 10 ⁵	d x 10 ⁹	n ^{IN} _i
H ₂	0.000	27.14	9.274	-1.381	7.645	56.36
CO	-2.420E+05	32.24	1.924	1.055	-3.596	12.56
CO ₂	-1.106E+05	30.87	-12.85	2.789	-12.72	8.27
CH ₄	-3.938E+05	19.80	73.44	-5.602	17.15	0.30
H ₂ O	-7.490E+04	19.25	52.13	1.197	-11.32	61.04

By substituting these values and those of the molar flow rates in the solving equation, one obtains:

$$\dot{H}_{IN}(\bar{n}_{IN}, T_{IN}) = 1.5405 \cdot 10^4 \cdot (823.15 - 298.15) + 3.0087 \cdot (823.15^2 - 298.15^2) + 1.8693 \cdot 10^{-3} \cdot (823.15^3 - 298.15^3) - 6.5888 \cdot 10^{-7} \cdot (823.15^4 - 298.15^4) - 1.0867 \cdot 10^8$$

$$\dot{H}_{IN}(\bar{n}_{IN}, T_{IN}) = -9.8117 \cdot 10^7 \text{ J/h}$$

$$\dot{H}_{OUT}(\bar{n}_{OUT}, T_{OUT}) = 1.9290 \cdot 10^4 \cdot (1073.15 - 298.15) + 3.5029 \cdot (1073.15^2 - 298.15^2) + 5.4366 \cdot 10^{-4} \cdot (1073.15^3 - 298.15^3) + 2.4286 \cdot 10^{-7} \cdot (1073.15^4 - 298.15^4) - 9.4917 \cdot 10^7$$

$$\dot{H}_{OUT}(\bar{n}_{OUT}, T_{OUT}) = -7.6583 \cdot 10^7 \text{ J/h}$$

On a basis of 100 mol/h, the heat supply results:

$$\dot{Q} = 2.1534 \cdot 10^7 \frac{\text{J}}{\text{h}}$$

In the case of 22.486 Nm³/h incoming methane, the heat supply is:

$$\dot{Q} = 2.1534 \cdot 10^7 \frac{\text{J}}{\text{h}} \cdot \frac{\text{h}}{100 \text{ mol}} \cdot \frac{22486 \text{ Nm}^3/\text{h}}{22.414 \cdot 10^{-3} \text{ Nm}^3/\text{mol}} = 2.160 \cdot 10^{11} \frac{\text{J}}{\text{h}} = 60.01 \text{ MW}$$