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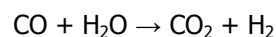
## Exercises of “Fundamentals of Chemical Processes”

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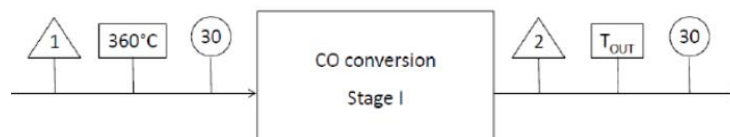
### Exercise 4

Outlet temperature and composition of a WGS reactor (Stage I) for the conversion of CO.

The gas stream that exits the second stage of a Reformer supplied with air is sent to a two-stage reactor for the conversion of CO, where the following reaction occurs (Water Gas Shift, WGS):



With reference to the first stage of the conversion of CO, it can be assumed that the reactor is adiabatic and that the outlet gases reach the thermodynamic equilibrium composition 20°C above the exit temperature  $T_{\text{OUT}}$ . Determine the temperature  $T_{\text{OUT}}$  and the composition of the exit composition.



#### **DATA:**

Stream 1:  $P = 30 \text{ atm}$   $T = 360^\circ\text{C}$

Stream 2:  $P = 30 \text{ atm}$   $T_{\text{OUT}} = ?$

Hypothesis: Ideal gas

WGS is at the chemical equilibrium

Adiabatic reactor

Species	Flow Rate (Nm <sup>3</sup> /h)	% Vol. Dry Basis
H <sub>2</sub>		56.36
N <sub>2</sub>		22.24
CO		12.56
CO <sub>2</sub>		8.27
Ar		0.27
CH <sub>4</sub>		0.3
H <sub>2</sub> O	73411	
Σ <sub>dry</sub>	120264	100.00
<b>Totale</b>	193675	

## Solution

The problem asks for the estimation of the composition and the temperature  $T_{OUT}$  of the gas stream that exits the reactor. In order to solve for these two unknowns, two equations must be written, namely the one derived from the equilibrium condition at the outlet of the reactor, and the enthalpy balance on the adiabatic reactor. It is convenient to write the mass balance by following the extent of reaction approach. The extent of reaction  $\lambda$  is defined and the outlet molar gas streams are determined as a function of the incoming ones, assuming a basis of 100 mol/h of incoming dry gas.

Species	Flow Rate (Nm <sup>3</sup> /h)	n <sup>in</sup> (mol/h)	n <sup>out</sup> (mol/h)
H <sub>2</sub>		56.36	56.36 + $\lambda$
N <sub>2</sub>		22.24	22.24
CO		12.56	12.56 - $\lambda$
CO <sub>2</sub>		8.27	8.27 + $\lambda$
Ar		0.27	0.27
CH <sub>4</sub>		0.3	0.3
H <sub>2</sub> O	73411	61.04	61.04 - $\lambda$
$\Sigma_{dry}$	120264	100.00	100.00 + $\lambda$
<b>Total</b>	<b>193675</b>	<b>161.04</b>	<b>161.04</b>

The amount of H<sub>2</sub>O is calculated as follows:

$$H_2O = \frac{73411}{120264} \cdot 100 = 61.04$$

Given that the WGS reaction reaches the thermodynamic equilibrium, the outlet composition must satisfy the equilibrium constraint:

$$k_{eq} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} = \frac{y_{CO_2} \cdot y_{H_2}}{y_{CO} \cdot y_{H_2O}} = \frac{n_{CO_2}^{out} \cdot n_{H_2}^{out}}{n_{CO}^{out} \cdot n_{H_2O}^{out}} = \frac{(56.36 + \lambda) \cdot (8.27 + \lambda)}{(12.56 - \lambda) \cdot (61.04 - \lambda)}$$

$$\ln k_{eq} = -\frac{\Delta G_R^0(T_{out} + 20)}{R \cdot (T_{out} + 20)}$$

It is worthy to note that the value of  $\lambda$  must be lower than 12.56 mol/h, in order for the calculation to maintain a physical meaning. In this way, the outlet composition is expressed as a function of the two unknown values of

the problem,  $\lambda$  and  $T_{OUT}$ . For the estimation of  $\Delta G^{\circ}_R(T)$ , the equation derived in Exercise 3 is used, leading to the following equation (Eq. 1):

$$-\frac{\Delta G^{\circ}_R(T^*)}{RT^*} = 5.040 + 4770.94 \cdot \frac{1}{T^*} - 1.945 \ln T^* + 5.631 \cdot 10^{-3} \cdot T^* - 2.170 \cdot 10^{-6} \cdot T^{*2} + 4.121 \cdot 10^{-10} \cdot T^{*3}$$

In the equation,  $T^* = T_{OUT} + 20$ .

The second equation required is the enthalpy balance on the reactor. Given that the reactor is adiabatic, one can write:

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

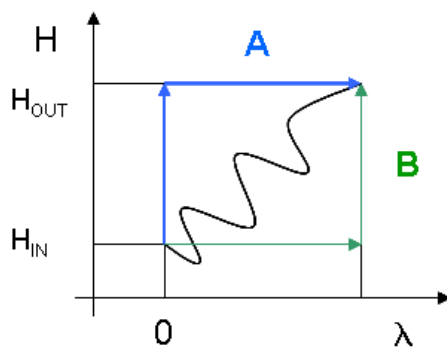
Different choices are possible to write this balance. For instance, if the enthalpy of the inlet gas at  $T_{REF} = T_{IN} = 360^{\circ}\text{C}$  is chosen as the reference, the inlet enthalpy is equal to zero:

$$\dot{H}_{IN}(\vec{n}_{IN}, T_{IN}) = 0$$

This leads the enthalpy balance to be written as follows:

$$H_{OUT} = 0$$

For the determination of  $H_{OUT}$ , it is useful to plot the enthalpy  $H$  as a function of the extent of the reaction  $\lambda$ :



$H_{OUT}$  can be calculated by following either the pathway **A** or **B**:

**A**: the enthalpy required to heat the incoming mixture from  $T_{IN}$  to  $T_{OUT}$  + the heat of reaction at  $T_{OUT}$

**B**: the heat of reaction at  $T_{IN}$  + the enthalpy required to heat the incoming mixture from  $T_{IN}$  to  $T_{OUT}$ . Given that the incoming composition is known, it is convenient to follow the pathway **A**. Hence:

$$\dot{H}_{OUT} = \int_{T_{IN}}^{T_{OUT}} \sum_{i=1}^{NC} n_i^{in} \cdot C_{p_i} dT + \lambda \cdot \Delta H_R^0(T_{out})$$

$$\Delta H_R^0(T_{out}) = \sum_{i=1}^{NC} \nu_i \left( \Delta H_{f,i}^0(T_{rif}) + \int_{298}^{T_{OUT}} C_{p_i} dT \right)$$

To determine the reaction enthalpy, for each of the species fed to the reactor (also those that do not react), the values of the parameters  $a_i$ ,  $b_i$ ,  $c_i$  and  $d_i$  of the polynomial equation of the specific heat at constant pressure  $C_p(T)$  are found in the thermodynamic property database.

Species	a	b x 10 <sup>3</sup>	c x 10 <sup>5</sup>	d x 10 <sup>9</sup>	n <sup>IN</sup> <sub>i</sub>
H <sub>2</sub>	27.14	9.274	-1.381	7.645	56.36
N <sub>2</sub>	31.15	-13.57	2.680	-11.68	22.24
CO	30.87	-12.85	2.789	-12.72	12.56
CO <sub>2</sub>	19.80	73.44	-5.602	17.15	8.27
Ar	20.80	0.000	0.000	0.000	0.27
CH <sub>4</sub>	19.25	52.13	1.197	-11.32	0.30
H <sub>2</sub> O	32.24	19.24	1.055	-3.596	61.04

Based on the flow rates of the inlet species, it can be calculated that:

$$\sum_{i=1}^{NC} n_i^{IN} \cdot a_i = 4753.23$$

$$\sum_{i=1}^{NC} n_i^{IN} \cdot b_i = 7.999 \cdot 10^{-1}$$

$$\sum_{i=1}^{NC} n_i^{IN} \cdot c_i = 3.523 \cdot 10^{-4}$$

$$\sum_{i=1}^{NC} n_i^{IN} \cdot d_i = -6.973 \cdot 10^{-8}$$

And also that:

$$\int_{T_{IN}}^{T_{OUT}} \sum_{i=1}^{NC} n_i^{IN} \cdot C_p \cdot dT = 4753.23 \cdot T_{OUT} + 4.000 \cdot 10^{-1} \cdot T_{OUT}^2 + 1.174 \cdot 10^{-4} \cdot T_{OUT}^3 - 1.743 \cdot 10^{-8} \cdot T_{OUT}^4 - 3.197 \cdot 10^6$$

The  $\Delta H_R$  as a function of the outlet temperature  $T_{OUT}$  is taken from Exercise 3:

$$\Delta H_R^0 = -39665.606 - 16.17 \cdot T_{OUT} + 4.682 \cdot 10^{-2} \cdot T_{OUT}^2 - 3.609 \cdot 10^{-5} \cdot T_{OUT}^3 + 1.028 \cdot 10^{-8} \cdot T_{OUT}^4$$

By substituting and rearranging the equation, the following form is obtained (Eq. 2):

$$(4753.23 - 16.17 \cdot \lambda) \cdot T_{OUT} + (4.000 \cdot 10^{-1} + 4.682 \cdot 10^{-2} \cdot \lambda) \cdot T_{OUT}^2 + (1.174 \cdot 10^{-4} - 3.609 \cdot 10^{-5} \cdot \lambda) \cdot T_{OUT}^3 + (-1.743 \cdot 10^{-8} + 1.028 \cdot 10^{-8} \cdot \lambda) - 39665.606 \cdot \lambda - 3.197 \cdot 10^6 = 0$$

By coupling Equation 1 and Equation 2, a system is obtained, which is non-linear and which allows for the determination of  $\lambda$  and  $T_{OUT}$ :

$$\begin{cases} f_1(\lambda, T_{OUT}) = 0 \\ f_2(\lambda, T_{OUT}) = 0 \end{cases}$$

The thermodynamic equilibrium constraint and the adiabaticity constraint allow to set up a system of two equations for the calculation of the two unknowns, which cannot be determined independently one of the other. An iterative procedure must be followed, starting from reasonable first attempt values, such as  $\lambda = 10$  mol/h and  $T_{OUT} = 680$  K. The solution of the system is:

$$\begin{cases} \lambda = 9.398 \text{ mol/h} \\ T_{OUT} = 698.96 \text{ K} \end{cases}$$

The required outlet composition is reported in the table below, with  $T_{OUT} = 698.96 \text{ K} = 425.81^\circ\text{C}$ :

Species	$n^{\text{out}}$ (mol/h)	% Vol. Dry Basis	% Vol. total
<b>H<sub>2</sub></b>	65.76	60.11	40.83
<b>N<sub>2</sub></b>	22.24	20.33	13.81
<b>CO</b>	3.16	2.89	1.96
<b>CO<sub>2</sub></b>	17.67	16.15	10.97
<b>Ar</b>	0.27	0.25	0.17
<b>CH<sub>4</sub></b>	0.30	0.27	0.19
<b>H<sub>2</sub>O</b>	51.64	-	32.07
<b><math>\Sigma_{\text{dry}}</math></b>	109.40	100.00	100.00

It is noteworthy that the enthalpy balance can be written with alternative forms, provided that they are coherent with that adopted in the exercise and with a reference state. For instance, the following choices are possible:

- 1) Assume a reference state, estimate the enthalpy of the reactants  $H_{IN}(T_{IN})$  and the enthalpy of the products  $H_{OUT}(T_{OUT})$  and then solve the equation:

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

- 2) Assume that the reaction occurs at the inlet temperature  $T_{IN}$  and is followed by the heating of the product gases from  $T_{IN}$  up to  $T_{OUT}$  (pathway B in the plot):

$$\lambda \cdot \Delta H_R(T_{IN}) + Q_{heating}(T_{IN}, T_{OUT}, \lambda) = 0$$

- 3) Assume that the reaction occurs at the outlet temperature  $T_{OUT}$  and is preceded by the heating of the inlet gases from  $T_{IN}$  up to  $T_{OUT}$  (pathway A in the plot):

$$Q_{heating}(T_{IN}, T_{OUT}, \lambda) + \lambda \cdot \Delta H_R(T_{OUT}) = 0$$

- 4) Choose the general approach with the reference state that sets the elementary species at  $T_{REF} = 298K$  and  $P = 1 \text{ atm}$ .