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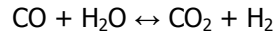
Exercises of “Fundamentals of Chemical Processes”

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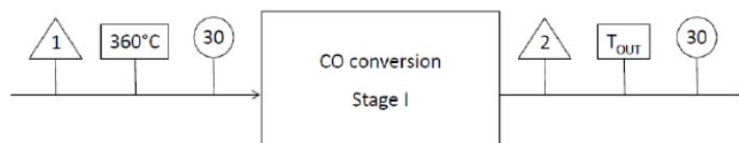
Exercise 3

Outlet temperature of a WGS reactor (Stage I) for the conversion of CO, applied for the abatement of CO to a fixed value.

The gas stream exiting 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 outlet gases reach the thermodynamic equilibrium composition at the exit temperature T_{OUT} . Determine the exit temperature T_{OUT} that allows for the amount of CO in the outlet gas stream to be equal to 0.39% (volume %) with respect to the dry current.



DATA:

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

Stream 2: $T_{\text{OUT}} = ?$ $P = 30 \text{ atm}$ $\text{CO}/\Sigma d_{ry} = 0.39\%$

Hypothesis: Ideal gas, WGS is at the chemical equilibrium

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

Solution

The approach with the extent of reaction is chosen to write the material balances. The basis for the material balances can be set to 100 mol/h of incoming dry gas. The extent of the reaction λ is defined and the composition of the outgoing species can be written, in terms of molar flow rates.

Species	Flow Rate (Nm ³ /h)	n ⁱⁿ (mol/h)	n ^{out} (mol/h)
H ₂		56.36	56.36 + λ
N ₂		22.24	22.24
CO		12.56	12.56 - λ
CO ₂		8.27	8.27 + λ
Ar		0.27	0.27
CH ₄		0.3	0.3
H ₂ O	73411	61.04	61.04 - λ
Σ_{dry}	120264	100.00	100.00 + λ
Total	193675	161.04	161.04

Given the 100 mol/h inlet dry gas basis, the amount of H₂O is calculated as follows:

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

The specific on the amount of CO in the outlet dry stream is used to calculate the extent of the reaction λ :

$$\frac{CO}{\Sigma_{dry}} = \frac{12.56 - \lambda}{100 + \lambda} = \frac{0.39}{100}$$

The equation leads to $\lambda = 12.1227$ mol/h. Once λ is calculated, the exit composition is readily derived:

Species	n ^{out} (mol/h)	% vol. n ^{out} dry basis	% vol. n ^{out}
H ₂	68.48	61.07	42.52
N ₂	22.24	19.84	13.81
CO	0.44	0.39	0.27
CO ₂	20.39	18.19	12.66
Ar	0.27	0.24	0.17
CH ₄	0.30	0.27	0.19
Σ_{dry}	112.12	100	-
H ₂ O	48.92	-	30.38

The exit composition is related to the outlet temperature via the hypothesis of thermodynamic equilibrium on the WGS reaction. In this case:

$$\Delta G_R(T) = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta G_R^0(T) + RT \cdot \ln k_{eq} = 0$$

It follows that:

$$\Delta G_R^0(T) = -RT \cdot \ln k_{eq}$$

In the case of the WGS reaction, assuming the ideal gas approximation, it is obtained:

$$k_{eq} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} = \frac{y_{CO_2} \cdot y_{H_2}}{y_{CO} \cdot y_{H_2O}} = \frac{n_{CO_2}^{out} \cdot n_{H_2}^{out}}{n_{CO}^{out} \cdot n_{H_2O}^{out}} = 65.29$$

$$\ln k_{eq} = 4.1788$$

The $\Delta G_R^0(298K)$ is calculated starting from the $\Delta G_{F,i}^0(298K)$ of the reactants and the products:

$$\Delta G_R^0(298K) = \sum_{i=1}^{NC} \nu_i \cdot \Delta G_{F,i}^0(298K)$$

In the equation, ν_i is the stoichiometric coefficient of the i-th specie in the reaction. In the same way, the $\Delta H_R^0(298K)$ is calculated as follows:

$$\Delta H_R^0(298K) = \sum_{i=1}^{NC} \nu_i \cdot \Delta H_{F,i}^0(298K)$$

$\Delta G_{F,i}^0(298K)$ and $\Delta H_{F,i}^0(298K)$ are found in the thermodynamic property database. The $\Delta G_R^0(T)$ at a T different from 298K is determined with the Van't Hoff and Kirchoff laws, which express the dependence of the ΔG^0 and the ΔH^0 from temperature.

$$\left. \frac{\partial (\Delta G^0(T)/RT)}{\partial T} \right|_p = - \frac{\Delta H^0(T)}{RT^2} \quad \text{Van't Hoff}$$

$$\left. \frac{\partial \Delta H^{\circ}(T)}{\partial T} \right|_p = \sum_1^{NC} \nu_i \cdot C_{p_i}(T) \quad \text{Kirchoff}$$

$$C_{p_i}(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^3$$

To derive the explicit expression of the $\Delta G_R^{\circ}(T)$ as a function of temperature T , the Kirchoff law is to be integrated first, starting from the reference temperature ($T_0 = 298\text{K}$), as follows:

$$\int_{T^{\circ}}^T \partial \Delta H_R^{\circ}(T) = \Delta H_R^{\circ}(298\text{K}) + \int_{T^{\circ}}^T \sum_1^{NC} \nu_i \cdot C_{p_i}(T) \cdot dT = \Delta H_R^{\circ}(298\text{K}) + \int_{T^{\circ}}^T (\Delta a + \Delta b \cdot T + \Delta c \cdot T^2 + \Delta d \cdot T^3) \cdot dT$$

$$a_{\text{tot}} = \sum_1^{NC} \nu_i \cdot a_i$$

$$b_{\text{tot}} = \sum_1^{NC} \nu_i \cdot b_i$$

$$c_{\text{tot}} = \sum_1^{NC} \nu_i \cdot c_i$$

$$d_{\text{tot}} = \sum_1^{NC} \nu_i \cdot d_i$$

$$\Delta H_R^{\circ}(T) = \Delta H_R^{\circ}(T_0) + a_{\text{tot}} \cdot (T - T_0) + \frac{b_{\text{tot}}}{2} \cdot (T^2 - T_0^2) + \frac{c_{\text{tot}}}{3} \cdot (T^3 - T_0^3) + \frac{d_{\text{tot}}}{4} \cdot (T^4 - T_0^4)$$

$$-\frac{\Delta G_R^{\circ}(T)}{RT} = -\frac{\Delta G^{\circ}(298)}{R \cdot T_0} + \int_{T_0}^T \frac{\Delta H_R^{\circ}(T)}{RT^2} dT$$

For each specie, the parameters of the specific heat are also found in the thermodynamic property database:

Specie	$\Delta H_F^{\circ}(298\text{K})$ [J/mol]	$\Delta G_F^{\circ}(298\text{K})$ [J/mol]	a	b x 10 ³	c x 10 ⁵	d x 10 ⁹	ν_i
H ₂	0.0	0.0	27.140	9.274	-1.381	7.645	+1
CO	-242000.0	-228800.0	32.240	1.924	1.055	-3.596	-1
CO ₂	-110600.0	-137400.0	30.870	-12.850	2.789	-12.720	+1
H ₂ O	-393800.0	-394600.0	19.800	73.440	-5.602	17.150	-1

C_p is J/mol/K. Given the data in the table above, the following equations are derived:

$$\sum_i^{NC} \nu_i \cdot C_p = -16.17 + 9.364 \cdot 10^{-2} \cdot T - 1.083 \cdot 10^{-4} \cdot T^2 + 4.111 \cdot 10^{-8} \cdot T^4$$

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

$$-\frac{\Delta G_R^0(T)}{RT} = 5.040 + 4770.94 \cdot \frac{1}{T} - 1.945 \ln T + 5.631 \cdot 10^{-3} \cdot T - 2.170 \cdot 10^{-6} \cdot T^2 + 4.121 \cdot 10^{-10} \cdot T^3$$

The solving equation is:

$$\ln k_{eq} = -\frac{\Delta G_R^0(T)}{RT}$$

$$4.1788 = 5.040 + 4770.94 \cdot \frac{1}{T} - 1.945 \ln T + 5.631 \cdot 10^{-3} \cdot T - 2.170 \cdot 10^{-6} \cdot T^2 + 4.121 \cdot 10^{-10} \cdot T^3$$

The equation is algebraic and implicit in the only unknown T ($f(T) = 0$), which can be solved with several either numeric (for instance, the bisection method or the Newton-Raphson method) or graphic methods. Solving the equation, one obtains:

$$T = 535.88 \text{ K} = 262.7^\circ\text{C}$$

A similar solution could have been obtained also by using linearized expressions of the $\Delta G_R^0(298\text{K})$ and the $\Delta H_R^0(298\text{K})$ given in some reference texts (for specific temperature ranges). For the WGS reaction:

$$\Delta G_R^0(T) = -9418 + 9.07 \cdot T \quad \Delta G_R^0(T) \text{ is cal/mol, } 300 \text{ K} < T < 600 \text{ K}$$

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

Using the first linearized equation, the following solving equation is obtained:

$$4.1788 = -\frac{-9418 + 9.07 \cdot T}{1.987 \cdot T}$$

In this case, $T = 542\text{K} = 269^\circ\text{C}$, given $R = 1.987 \text{ cal/mol/K}$.