Equilibrium Composition of the Steam Reforming of Natural Gas

This application calculates the equilibrium composition of the steam reforming of natural gas. The reaction scheme is:

$$CH_4 + H_2O \rightleftarrows CO + 3\ H_2$$
$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The Gibbs energy of the equilibrium composition is parametrized with respect to the number of moles of each component. This expression is minimized to find the equilibrium composition.

Parameters

Pressure $P_c := 40 \cdot 10^5\ Pa$

Standard pressure $P_s := 10^5\ Pa$

Gas constant $R := 8.31433\ J \cdot mol^{-1} \cdot K^{-1}$

Temperature $T := 1100\ K$

Gibbs Energy of the Equilibrium Mixture

Gibbs energy of the individual components

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Property := ThermophysicalData:-Chemicals:-Property
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$G_{CH4} := \mathrm{Property}(Gmolar, \text{"CH4(g)"}, temperature = T) + T \cdot R \cdot \ln(P_c / P_s)$

$G_{H2O} := \mathrm{Property}(Gmolar, \text{"H2O(g)"}, temperature = T) + T \cdot R \cdot \ln(P_c / P_s)$

$G_{CO} := \mathrm{Property}(Gmolar, \text{"CO(g)"}, temperature = T) + T \cdot R \cdot \ln(P_c / P_s)$

$G_{H2} := \mathrm{Property}(Gmolar, \text{"H2(g)"}, temperature = T) + T \cdot R \cdot \ln(P_c / P_s)$

$G_{CO2} := \mathrm{Property}(Gmolar, \text{"CO2(g)"}, temperature = T) + T \cdot R \cdot \ln(P_c / P_s)$

Total Gibbs energy $gibbs := n_1 \cdot \left(G_{CH4} + R \cdot T \cdot \ln\left(\frac{n_1}{n_t}\right)\right) + n_2 \cdot \left(G_{H2O} + R \cdot T \cdot \ln\left(\frac{n_2}{n_t}\right)\right) + n_3 \cdot \left(G_{CO} + R \cdot T \cdot lr\right.$

Constraints

Equate the number of moles of components $CH_4 + 3.2\ H_2O = n_1 \cdot CH_4 + n_2 \cdot H_2O + n_3 \cdot CO + n_4 \cdot H_2 + n_5 \cdot CO_2$

Total number of moles $n_t := n_1 + n_2 + n_3 + n_4 + n_5$

Balance on C $con_1 := n_1 + n_3 + n_5 = 1\ \mathrm{mol}$

Balance on H $con_2 := 4 \cdot n_1 + 2 \cdot n_2 + 2 \cdot n_4 = 4\ \mathrm{mol} + 6.4\ \mathrm{mol}$

Balance on O $con_3 := n_2 + n_3 + 2 \cdot n_5 = 3.2\ \mathrm{mol}$

Minimize the Gibbs Energy via Optimization

Minimize the Gibbs Energy

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res := Optimization:-Minimize(gibbs, {con₁, con₂, con₃}, initialpoint
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$res = [-4.790 \times 10^5\ \mathrm{J}, [n_1 = 0.332\ \mathrm{mol}, n_2 = 2.209\ \mathrm{mol}, n_3 = 0.345\ \mathrm{mol}, n_4$

Check on constraints

$eval(con_1, res[2]) = 1.000\ \mathrm{mol} = 1\ \mathrm{mol}$

$eval(con_2, res[2]) = 10.400\ \mathrm{mol} = 10.400\ \mathrm{mol}$

$eval(con_3, res[2]) = 3.200\ \mathrm{mol} = 3.200\ \mathrm{mol}$

Minimize the Gibbs Energy via Lagrange Multipliers

$$eqComposition_1 := L_1 \cdot \frac{\partial}{\partial n_1} lhs(con_1) + L_2 \cdot \frac{\partial}{\partial n_1} lhs(con_2) + L_3 \cdot \frac{\partial}{\partial n_1} lhs(con_3) =$$

$$eqComposition_2 := L_1 \cdot \frac{\partial}{\partial n_2} lhs(con_1) + L_2 \cdot \frac{\partial}{\partial n_2} lhs(con_2) + L_3 \cdot \frac{\partial}{\partial n_2} lhs(con_3) =$$

$$eqComposition_3 := L_1 \cdot \frac{\partial}{\partial n_3} lhs(con_1) + L_2 \cdot \frac{\partial}{\partial n_3} lhs(con_2) + L_3 \cdot \frac{\partial}{\partial n_3} lhs(con_3) =$$

$$eqComposition_4 := L_1 \cdot \frac{\partial}{\partial n_4} lhs(con_1) + L_2 \cdot \frac{\partial}{\partial n_4} lhs(con_2) + L_3 \cdot \frac{\partial}{\partial n_4} lhs(con_3) =$$

$$eqComposition_5 := L_1 \cdot \frac{\partial}{\partial n_5} lhs(con_1) + L_2 \cdot \frac{\partial}{\partial n_5} lhs(con_2) + L_3 \cdot \frac{\partial}{\partial n_5} lhs(con_3) =$$

$res2 := fsolve(\{eqComposition_1, eqComposition_2, eqComposition_3, eqCompositio$

$res2 = \{L_1 = -1.324 \times 10^4\ \frac{\mathrm{J}}{\mathrm{mol}}, L_2 = 1.291 \times 10^4\ \frac{\mathrm{J}}{\mathrm{mol}}, L_3 = -1.875 \times 10^5\ \frac{\mathrm{J}}{\mathrm{mol}}, n_1 =$

$$\ln\left(\frac{n_3}{n_t}\right)\Bigg) + n_4\cdot\left(G_{H2} + R\cdot T\cdot \ln\left(\frac{n_4}{n_t}\right)\right) + n_5\cdot\left(G_{CO2} + R\cdot T\cdot \ln\left(\frac{n_5}{n_t}\right)\right)$$

t = {n_1 = 1 mol, n_2 = 1 mol, n_3 = 1 mol, n_4 = 1 mol, n_5 = 0.6 mol}, assume = nonnegative)

= 2.327 mol, n_5 = 0.323 mol]]

$$\frac{d}{dn_1}\text{gibbs}$$

$$\frac{d}{dn_2}\text{gibbs}$$

$$\frac{d}{dn_3}\text{gibbs}$$

$$\frac{d}{dn_4}\text{gibbs}$$

$$\frac{d}{dn_5}\text{gibbs}$$

$_4$, eqComposition$_5$, con$_1$, con$_2$, con$_3$}, {L_1 = −100 J·mol^{-1}, L_2 = −100 J·mol^{-1}, L_3 = 1 J·mol^{-1}, n_1 = 1 mol, n_2 =

0.332 mol, n_2 = 2.209 mol, n_3 = 0.345 mol, n_4 = 2.327 mol, n_5 = 0.323 mol}

$1\ \mathtt{mol}, n_3 = 1\ \mathtt{mol}, n_4 = 1\ \mathtt{mol}, n_5 = 1\ \mathtt{mol}\})$