Under stoichiometric methane combustion

When methane burns under stoichiometrically ($\lambda = a < 1$), there is insufficient amount of oxygen and the flue gas will contain multiple gas species, as shown in the following equation:

$$CH_4 + 2a(O_2 + 3.76N_2) \rightarrow bCO_2 + cCO + dH_2O + eH_2 + 2a \cdot 3.76N_2$$

The amounts of gases CO_2, CO, H_2O and H_2 in the combustion products can be solved using chemical equilibrium assumption. The governing equation set is:

C atom balance:	$b + c - 1 = 0$	Eq. 1
O atom balance:	$2b + c + d - 4a = 0$	Eq. 2
H atom balance	$d + e - 2 = 0$	Eq. 3
Water-Gas Shift equilibrium reaction:	$dc \cdot K_p(T) - be = 0$	Eq. 4

where the equilibrium constant K_p depends on temperature and is defined as:

$$K_p(T) = e^{0.31688+4.1778z+0.63508z^2-0.29353z^3}, \qquad z = \frac{1000}{T} - 1$$

The equation set contains three linear algebraic equations and one nonlinear algebraic equation. It can be solved for example using **fsolve** for known air-fuel ratio a and temperature T.

a) Solve the equilibrium composition of the combustion products for $a = \lambda = 0.8$, when the combustion products are in temperature $T = 1600\ K$.
b) Make a graph which shows the equilibrium composition for $0.3 \leq a \leq 1$, when the combustion products are in temperature $T = 1600\ K$.

Use the following notation in your Python code:

$$n = \begin{bmatrix} n_{CO_2} \\ n_{CO} \\ n_{H_2O} \\ n_{H2} \\ n_{N_2} \end{bmatrix} = \begin{bmatrix} b \\ c \\ d \\ e \\ 2a \cdot 3.76 \end{bmatrix} \quad \text{(mol)}$$

<u>Result validation:</u> From Eq. (1) in the following page, we can calculate the flue gas composition with $\lambda = 1$:

$$n_{tot} = n_{CO_2} + n_{H_2O} + n_{N_2} = 1 + 2 + 2 \cdot 3.76 = 10.52\ mol$$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{tot}} = \frac{1\ mol}{10.52\ mol} = 9.51 \text{ mol-\%} = 9.5 \text{ vol-\%}$$

$$x_{H_2O} = \frac{n_{H_2O}}{n_{tot}} = \frac{2\ mol}{10.52\ mol} = 19.0 \text{ vol-\%}$$

$$x_{N_2} = \frac{n_{N_2}}{n_{tot}} = \frac{2 \cdot 3.76\ mol}{10.52\ mol} = 71.5 \text{ vol-\%}$$

In part b), check that your flue gas composition approaches this composition when $\lambda \rightarrow 1$.

Detailed derivation of the problem

Stoichiometric methane combustion reaction with air ($\lambda\ =\ 1$):

$$CH_4\ +\ 2(O_2\ +\ 3.76N_2) \rightarrow CO_2\ +\ 2H_2O + 2 \cdot 3.76N_2 \quad (1)$$

In under stoihiometric conditions there is not enough oxygen to burn all methane to CO_2 and H_2O. Because of the lack of oxygen, there will be also CO and H_2 in the combustion products. The reaction equation is then:

$$CH_4\ +\ 2a(O_2\ +\ 3.76N_2) \rightarrow bCO_2\ +\ cCO\ +\ dH_2O\ +\ eH_2\ +\ 2a \cdot 3.76N_2 \quad (2)$$

Here the variable a is the air-fuel ratio ($a = \lambda$). In under stoichiometric conditions $a < 1$. How can we estimate how the insufficient oxygen molecules divide between the different gases? In other words, how do we solve the composition of the combustion products (b, c, d and e)?

If we assume that the gases have enough time to react in the combustion chamber, the composition will reach equilibrium. The equilibrium composition can be solved using the Water-Gas Shift (WGS) equilibrium reaction. It tells us the equilibrium composition between CO, H_2O, CO_2 and H_2 molecules.

$$CO + H_2O\ \leftrightarrow CO_2 + H_2 \qquad \text{Equilibrium constant } K_p = K_p(T) \qquad (2)$$

For WGS reaction, the equilibrium constant is defined as:

$$K_p = \frac{p_{CO2}p_{H2}}{p_{H2O}p_{CO}} = \frac{\left(\frac{b}{n_{tot}}p_{tot}\right)\left(\frac{e}{n_{tot}}p_{tot}\right)}{\left(\frac{d}{n_{tot}}p_{tot}\right)\left(\frac{c}{n_{tot}}p_{tot}\right)} = \frac{be}{dc}$$

Where b, c, d and e are the amounts (in mol) of CO_2, CO, H_2O and H_2 in equilibrium when 1 mol of methane combusts. The equilibrium constant is a function of temperature and could be calculated using the standard state entropies and enthalpies of the gas species. Twigg 1989 provides a correlation that can be readily used:

$$K_p(T) = e^{0.31688+4.1778z+0.63508z^2-0.29353z^3}, \qquad z = \frac{1000}{T} - 1$$

We can solve the equilibrium composition when we add molecule balance equations to our equation set:

$$C\ atom\ balance: 1 = b + c$$

$$O\ atom\ balance: 2 \cdot 2a = 2b + c + d$$

$$H\ atom\ balance: 4 = 2d + 2e$$

To understand these atom balances, look at Eq. (2) and equate the amount of atoms on the left and right hand side of the equation.

Finally, we have a set of algebraic equations which can be solved to obtain the equilibrium composition of the combustion products:

C atom balance:	$b + c - 1 = 0$	Eq. 1
O atom balance:	$2b + c + d - 4a = 0$	Eq. 2
H atom balance	$d + e - 2 = 0$	Eq. 3
Equilibrium reaction:	$\frac{be}{dc} = K_p(T) \;\rightarrow\; dc \cdot K_p(T) - be = 0$	Eq. 4

The equation set contains three linear algebraic equations and one nonlinear algebraic equation. It can be solved for example using **fsolve** for known air-fuel ratio a and temperature T.