1st Law combustion problems

Consider this problem: Say we are burning propane (C_3H_8) in a constant-pressure reactor. We want to mix in a sufficient amount of secondary air to the combustion to limit the combustion product temperature to \( T_p = 1900 \) K. Determine the overall equivalence ratio \( \Phi \) of the combustion process.

We will assume that the process is adiabatic, and that there is negligible KE in the flow. Assume also that fuel and air enter at room temperature, i.e., 298 K (we would need to know this!)

The 1st law has (no work, \( Q = 0 \), SSSF)

\[
H_r = H_p \tag{1}
\]

i.e., the enthalpy \( h \) of the process is constant.

Assume complete combustion. The overall reaction is

\[
C_3H_8 + \frac{5}{\Phi} (O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(\frac{1}{\Phi} - 1)O_2 + \frac{19.80}{\Phi} N_2 \tag{2}
\]

Reactants are at 298 K, so

\[
H_r = \bar{H}_{C_3H_8}^\circ + \frac{5}{\Phi} (\bar{H}_{O_2}^\circ + 3.76 \bar{H}_{N_2}^\circ) = -103.8 \text{ MJ}
\]
For the products (using the gas props data sheet @ 1800K)

\[ \bar{h}_{\text{CO}_2} = -319 \text{ MJ, } \bar{h}_{\text{H}_2} = -179 \text{ MJ, } \bar{h}_\text{O}_2 = 51.8 \text{ MJ, } \bar{h}_\mu = 49 \text{ MJ} \]

(per mol). So

\[ \Delta H_p = 3 \cdot \bar{h}_{\text{CO}_2} + 4 \cdot \bar{h}_{\text{H}_2} + 5(2-1) \cdot \bar{h}_\text{O}_2 + \frac{18.8}{\phi} \cdot \bar{h}_\mu \]

\[ = -1917 \cdot \phi + 1180 \text{ MJ} \]

One from eq (1): \[ h_p - h_r = 0 \] or

\[ -104 - (-1917 \cdot \phi + 1180) = 0 \Rightarrow \phi = 0.651 \]

Or, \[ \phi = 1.54 = 154\% \] theoretical air = 54\% excess air.

Solution to this problem is fairly straightforward. We know the temperatures of the reactants and the products, and enthalpy values for the various species can be looked up directly from the tables.

We can use a somewhat simpler approach to estimate the required \( \phi \). Recall that enthalpy can be separated into chemical and sensible (temperature) parts, so

\[ \Delta H = 0 \text{ (adiabatic)} = \Delta H_{\text{chem}} + \Delta H_{\text{sensible}} \]
Now 1 kmol of fuel goes into the reaction, according to eqn (2). So

$$\Delta H_{\text{chem}} = -1 \text{ kmol} \cdot \text{LHV} = -1 \times 14,604 \frac{\text{kJ}}{\text{kg}} \times 100.1 \frac{\text{kg}}{\text{kmol}}$$

$$= -2046 \text{ MJ} \quad \text{(data from Turner, p. 699)}$$

$$\Delta H_{\text{sensible}} = N \cdot \overline{C_p} \cdot \Delta T$$

where \( N \) = # of kmoles in mix, \( \overline{C_p} \): average molar specific heat of mix, and \( \Delta T \): temperature change. \( \Delta T = 1800 - 298 = 1502 \text{ K} \). The products are mostly \( \text{N}_2 \), so use \( \overline{C_p} \approx \overline{C_p, \text{N}_2} \) at \( T_{\text{ave}} = 1000 \text{ K} \):

$$\overline{C_p} = 32.8 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \quad \text{(Table A.7)}. \text{ From eq. (2):}$$

$$N = 3 + 4 + 5(\frac{1}{\phi} - 1) + \frac{18.8}{\phi} = 2 + \frac{23.8}{\phi}$$

Now use the above in (3):

$$\left(2 + \frac{23.8}{\phi}\right) \cdot 32.8 \cdot 1502 = 2046 \cdot 10^3 \quad \text{or}$$

$$\phi = 0.602$$

The biggest source of error in this approach is our value of \( \overline{C_p} \). We underestimate \( C_p \) when we approximate it by the \( \text{N}_2 \) value; triatomic molecules (\( \text{CO}_2, \text{H}_2\text{O} \)) have a larger \( C_p \) than diatomic molecules.
Flame temperature calculation: The typical problem here is when we have reactants, at a specified temperature and equivalence ratio, combusting in an adiabatic combustor. We want to predict the product temperature (i.e., the flame temperature).

Since the process is adiabatic, the 1st law will be the same as eq (1). We can calculate \( H_p \) since we know \( T_r \) and \( \phi \), and the 1st law gives us \( H_p = H_r \). We now have to find the temperature using \( H_p \).

This problem can be tedious if we are using the tables. As an example, say the fuel is propane, \( \phi = 0.8 \), and \( T_r = 298 \) K. Assume complete combustion:

\[
C_3H_8 + \frac{5}{2}(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 1.25O_2 + 23.5N_2
\]

\( H_r = -103.8 \text{ MJ} \) (same calculation as before)

\[
H_p = \left[ 3h_{CO_2} + 4h_{H_2O} + 1.25h_{O_2} + 23.5h_{N_2} \right] \text{ @ } T_p
\]

Say \( T_p = 2000 \) K: using the property data sheet:

\[
H_p = -3 \cdot 302 - 4 \cdot 169 + 1.25 \cdot 59 + 23.2 \cdot 56 = -209.1
\]

\( \Delta H = H_p - H_r = -105.3 \text{ MJ} \)
For $T_p=2000^\circ K$ we get $\Delta H < 0$, which implies that heat would be transferred from the system. The product temperature is therefore too low.

Try $T_p=2200^\circ K$:

$$H_p = -3.290 - 4.159 + 1.25 \times 67 + 23.5 \times 63.3 = 65.3 \text{ MJ}$$

so $\Delta H = 65.3 - (-103.8) = 169.1 \text{ MJ}$

Since $\Delta H < 0$, heat would have to flow into the products to maintain $T_p$ at 2200 K. The product temperature is too high.

We can interpolate the results to get $T_p @ \Delta H = 0$.

$$T_p = T_p_1 + \left( T_p_2 - T_p_1 \right) \frac{\Delta H^0 - \Delta H_1}{\Delta H_2 - \Delta H_1} = 2000 + 200 \times \frac{-(-103.3)}{169.1 - (-105.3)}$$

$$= 2077 \text{ K}$$

There's not much sense trying to get more accuracy out of the calculation - by interpolating the table $h$ values @ 2077 K. We have assumed complete combustion in this calculation - and this approximation will be questionable at the high product temperature because of chemical dissociation (i.e., molecules breaking apart).
A detailed equilibrium calculation using the STANJAN code (which we'll discuss later) gives $T_p = 2042 \text{ K}$.

We can also approximate the temperature using a constant $C_p$ assumption. From Eq. (3),

$$\Delta H = \Delta H_{\text{chem}} + \Delta H_{\text{total}}$$

$$= -LHV + nC_p(T_p - T_R) \quad \text{(per kmol of C}_3\text{H}_8)$$

$$n = 3 + 4 + 1.25 + 23.5 = 31.75$$

$$C_p \approx 23 \text{ kJ/kmol} \quad \text{(N}_2\text{ value)}$$

$$T_p = T_R + \frac{LHV}{nC_p} = 298 + \frac{2046 \times 10^3}{31.75 - 33} = 2251 \text{ K}$$

This answer is way off - mostly because we have a poor choice for $C_p$.

**Closed Systems: Control Mass**

The first law for a closed system (such as a piston-cylinder system) is

$$\Delta U = Q_{1-2} - W_{1-2}$$

Say we have a mix of C$\text{}_3$H$\text{}_8$ and air in a rigid, adiabatic vessel, with $Q = 1$ and $T_R = 298 \text{ K}$, $P_R = 1 \text{ atm}$. The mix is ignited. Find $T_p$ and $P_p$. 

Since the system is rigid, then $V = \text{const}$ and $W_{1-2} = 0$. Also $Q_{1-2} = 0$ since the system is adiabatic. So $U_p = U_R$.

Assume complete combustion (a poor approximation, it will turn out). The reaction is

$$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

$$U_R = \overline{U}_{C_3H_8} + 5(\overline{U}_{O_2} + 3.76\overline{U}_{N_2}) \quad @ \quad 298 \, K$$

Now $\overline{U} = \overline{h} - p\overline{V} = \overline{h} - RT$ (for ideal gases), so

$$U_R = \overline{h}_{C_3H_8} + 5(\overline{h}_{O_2} + 3.76\overline{h}_{N_2}) - (1 + 5 (1 + 3.76))RT_k$$

$$-103.8 \times 10^3 - 24.8 \times 8.314 \times 298 = -165.2 \times 10^3 \, kJ$$

$$U_p = 3\overline{U}_{CO_2} + 4\overline{U}_{H_2O} + 18.8\overline{U}_{N_2} \quad @ \quad T_p$$

We could use the same $\overline{U} = \overline{h} - RT$ approach as above, or we can simply look up $\overline{U}$ from the proper data sheet.

At $T_p = 3000 \, K$

$$U_p = 3 \times 266 - 4 \times 410 + 18.8 \times 67.8 = -93.4 \, MJ$$
So $\Delta U = -83.4 - (-165.2) = 81.8 \text{ J}$; $T_p$ too high

At $T_p = 2900$ K:

$U_p = -3 \cdot 271 - 4 \cdot 145 + 18.8 \cdot 65 = -171 \text{ MJ}$

$\Delta U = -171 - (-165.2) = -5.8 \text{ MJ} \approx$ pretty close

So, our complete combustion approximation is $T_p \approx 2900$ K. Molecule dissociation will be significant at this temperature, and we'll need to perform a detailed equilibrium calculation (using STANJAN) to get a more accurate result.

Since $V$ is cont. and assuming ideal gas behavior,

$V = \frac{n_R R \alpha T \bar{R}}{P_R} = \frac{n_p R \alpha T_p}{P_p}$, so

$P_p = P_R \cdot \frac{n_p T_p}{n_R T \bar{R}} = 1 \cdot \frac{25.8 \cdot 2900}{24.8 \cdot 298} = 10.1 \text{ atm}$