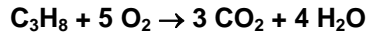


Chemical reactions and Combustion

Until now, we limited our study to non-reacting systems: the chemical composition remains unchanged during the process. In a process involving combustion, new components are created and others are destroyed. It is important, therefore, to take into account the energy needed to create or destroy these components.

Let us take a simple example: Combustion of propane (C_3H_8) in a pure oxygen environment:



To balance this reaction, the number of atoms of an element must remain the same before, after and during the chemical reaction. Note that during a chemical reaction there is a conservation of mass and number of atoms but not a conservation of the total number of moles (for the combustion of propane: 6 moles on the left side compared to 7 moles on the right side).

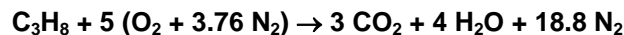
In this introduction to chemical reactions and combustion, we will consider a **complete combustion**, i.e, the products of the combustion of an hydrocarbon fuel will be **H_2O and CO_2** . An **incomplete combustion** will result in products that contain **H_2 , CO , C or OH** . The causes of incomplete combustion are usually: insufficient oxygen or insufficient mixing.

For the above example, we hypothesized a combustion in a pure oxygen environment, which is obviously not the case in practice. In practice, air is used for combustion. Here, we will assume that air consists of 21% O_2 and 79% N_2 by volume. So for each mole of O_2 involved in the reaction, we will have:

$$\frac{79}{21} = 3.76 \frac{mol N_2}{mol O_2}$$

And for air we will have: 1 kmol O_2 + 3.76 kmol N_2 = 4.76 kmol of air

But, as N_2 will not undergo any chemical reaction, the combustion of propane with air can be written under the following form:



When analyzing a chemical reaction, the components that exist before the reaction are called reactants (C_3H_8 ; O_2 and N_2) and the components that exist after the reaction are called products (CO_2 ; H_2O and N_2).

Complete combustion of an hydrocarbon does not occur with any amount of air, in fact, a minimum amount of air that supplies O_2 is required. This amount of air is called: theoretical air.

In practice however, the amount of air used is higher than the theoretical air. This is to increase the chances of complete combustion or to control the temperature of the combustion chamber. The amount of air in excess is called: ... excess air ... (what a surprise!!!). When we say **50%** excess air, you must understand that we used $100\%+50\%=150\%$ of theoretical air.

As you may notice, the combustion of hydrocarbon fuels involves H_2O . The calculation of the dew point of the products is often of interest, because if the temperature drops below the dew point, the water vapor begins to condensate. This is not suitable, since this water droplets can combine with sulfure dioxide (SO_2) that may be present in the combustion gases, forming sulfuric acid (H_2SO_4), which is very corrosive.

Air-Fuel ratio (AF)

The parameter that relates the amount of air used in a combustion process is the air-fuel ratio (AF)

$$AF = \frac{\text{mass of air}}{\text{mass of fuel}} = \frac{m_a}{m_f}$$

As an example, for the above reaction, the AF for theoretical air is:

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{5(4.76)(29)}{1(44)} = 15.69 \frac{kg \text{ air}}{kg \text{ fuel}}$$

if we use an AF higher than 15.69, we are using a lean mixture. And if AF is less than 15.69, we are using a rich mixture.

Example

Butane is burned with dry air-fuel ratio of 20. Calculate:

- The percentage of excess air.
- The molar percentage of CO₂ in the products.
- The dew-point temperature of the products.

Enthalpy of formation and enthalpy of combustion

When a chemical reaction occurs, there may be considerable change in the chemical composition of a system. Thus, it will be problematic to define a control volume for the mixture: the input and the output are not the same components.

Furthermore, for the analysis of a single component, we do not have to worry about our reference for enthalpy, since for a process, we are interested in computing the variation in enthalpy and our reference enthalpy will be canceled.

$$\Delta h = (h_2 - h_{ref}) - (h_1 - h_{ref}) = h_2 - h_1$$

but, in combustion, the components are not the same at state 1 and 2. Therefore:

$$\Delta h = (h_2 - h_{ref 2}) - (h_1 - h_{ref 1}) \neq h_2 - h_1$$

the reference enthalpy for each component is taken as its enthalpy at 25°C and 1 atm and this state will be denoted h°.

And to compute enthalpy at a different temperature, follow this example for the enthalpy of N₂ at 500 K is:

$$\bar{h}_{500K} - \bar{h}^0 = 14581 - 8669 = 5912 \text{ kJ / kmol [from table A-18; page 851]}$$

Note 1: in chemical reactions, it is more convenient to work with quantities per mole (or kmol).

Note 2: some components exist at two phases at 25°C. The phase must be, therefore, specified: H₂O (l) for liquid water and H₂O (g) for vapor water.

Enthalpy of formation

The enthalpy of formation is the enthalpy change when a component is formed, denoted (h_f°). The enthalpies of formation of numerous components are listed in tables. Note that some components have a positive enthalpy of formation, indicating that they require energy to form (an endothermic reaction); others have a negative enthalpy of formation, indicating that they give off energy when they are formed (a exothermic reaction).

Enthalpy of combustion

It represents the amount of heat released during a steady state combustion process when 1 kmol of fuel is burned completely at a certain temperature and pressure.

Exp:

Enthalpy of formation for H₂ = 0 (H₂ is a stable component that exists under this form in nature)
 Enthalpy of combustion for H₂ (to form H₂O) = 285 830 kJ/kmol

Remark: If the products of combustion contains liquid water, the enthalpy of combustion is the higher heating value (HHV), and if the products contain water vapor, the enthalpy of combustion is the lower heating value (LHV). The difference between HHV and LHV is the heat of vaporization \bar{h}_{fg} .

Applying the first law to combustion processes:

Before applying the first law to a combustion process, it is convenient to write the enthalpy of a component in a form suitable for use for reacting systems:

$$\text{Enthalpy} = \underbrace{\bar{h}_f^0}_{\text{formation}} + \left(\underbrace{\bar{h}}_{\text{actual}} - \underbrace{\bar{h}^0}_{\text{reference}} \right)$$

the first law can be written for an open system as:

$$Q_{in} + W_{in} + \underbrace{\sum N_r \left(\bar{h}_f^0 + (\bar{h} - \bar{h}^0) \right)}_{H_r} = Q_{out} + W_{out} + \underbrace{\sum N_p \left(\bar{h}_f^0 + (\bar{h} - \bar{h}^0) \right)}_{H_p}$$

N_r and N_p are the number of moles of the reactant or the product per mole of fuel.

And, the first law can be written for a closed system as:

$$Q_{in} + W_{in} + \underbrace{\sum N_r \left(\bar{h}_f^0 + (\bar{h} - \bar{h}^0 - P\bar{v}) \right)}_{H_r} = Q_{out} + W_{out} + \underbrace{\sum N_p \left(\bar{h}_f^0 + (\bar{h} - \bar{h}^0 - P\bar{v}) \right)}_{H_p}$$

where the internal energy is expressed as a function of enthalpy ($u=h-Pv$), pressure and specific volume. The choice of this form (with enthalpy rather than internal energy) is justified by the fact that enthalpy is tabulated.

For an ideal gas: $P\bar{v}$ can be replaced by $R_u T$.

In the above relations, we employ one of the following methods to find $(\bar{h} - \bar{h}^0)$:

- For a solid or a liquid:

Use $\bar{C}_p \Delta T$

- For gases: several methods can be applied, however the easiest one is:

Assume an ideal gas and use tabulated values for \bar{h} .

Example [Cengel page 717]

Liquid propane (C_3H_8) enters a combustion chamber at $25^\circ C$ at a rate of 0.05 kg/min where it is mixed and burned with 50% excess air that enters the combustion chamber at $7^\circ C$. An analysis of combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 90% of the carbon burns to CO_2 , with the remaining 10% forming CO . If the exit temperature of the combustion gases is 1500 K, determine:

- The mass flow rate of air.
- The rate of heat transfer from the combustion chamber.

Adiabatic flame temperature:

If we consider a combustion process that takes place adiabatically, with no work or changes in kinetic and potential energies, the chemical energy released will be used only to raise the temperature of the combustion products, in this particular case, the temperature reached by the products is called: adiabatic flame temperature.

The adiabatic flame temperature is a function of excess air and it is maximal for 0% excess air, and thus for theoretical air.

Hence, the higher is excess air the lower will be the adiabatic flame temperature. As a practical consequence, excess air can be used to reach an adiabatic flame temperature lower than the maximum allowable blade turbine temperature (as an example).

The computation of the adiabatic flame temperature must be performed under the following assumptions:

- Complete combustion.
- No heat transfer from the combustion chamber.
- No dissociation of the products into other chemical species.

Applying the first law under these assumptions gives:

$$H_{\text{Prod}} = H_{\text{React}}$$

$$\sum N_P (\bar{h}_f^o + \bar{h} - \bar{h}^o)_P = \sum N_R (\bar{h}_f^o + \bar{h} - \bar{h}^o)_R$$

the calculation of the enthalpy of the products H_{Prod} is not straightforward, since the temperature of the products is not known prior to the calculation (it is exactly what we are looking for).

An iterative process has to be used, by considering as a first guess all the product gases are nitrogen (N_2).

Example

Propane is burned with 250% theoretical air, both are at 25°C and 1 atm. Predict the adiabatic flame temperature in the steady flow combustion chamber.

Entropy change of reacting systems

The entropy balance for any system undergoing any process can be expressed as:

$$\underbrace{S_{in} - S_{out}} + \underbrace{S_{gen}} = \underbrace{\Delta S_{system}}$$

Net entropy transfer by heat and mass Entropy generation Change in entropy

or:

$$\sum \frac{Q_k}{T_k} + S_{gen} = S_{Prod} - S_{React}$$

Where T_k is the temperature at the boundary where Q_k crosses it.

For an adiabatic process ($Q=0$):

$$S_{gen,adiabatic} = S_{Prod} - S_{React}$$

This expression includes the entropy of the components (CO_2 ; O_2 ; ...) not the variation in entropy and therefore it is essential to determine a common base for the entropy of all the substances (as we did with enthalpy).

Third law of thermodynamics

“ The entropy of a pure crystalline substance at absolute zero temperature is zero”

$$S|_{T=0K} = 0$$

the entropy values relative to this common base are called the **absolute entropy** \bar{S}^o .

To compute the entropy generation using the above expression, the absolute entropy of several components (CO_2 ; O_2 ; N_2 ...) are listed in tables at 1 atm. However, entropy is more complex than enthalpy, since even under the assumption of an ideal gas, the entropy is a function of both T and P (the enthalpy depends only on T).

Therefore, the entropy of a component within a mixture **MUST BE COMPUTED USING ITS PARTIAL PRESSURE**

For a component (i) within a mixture:

$$\bar{S}_i(T, P_i) = \underbrace{\bar{S}_i^o\left(T, \overset{=1\text{atm}}{\bar{P}}_0\right)}_{\text{from table}} - R_U \ln\left(\frac{y_i P_m}{P_0}\right)$$

P_m is the pressure of the mixture.

Second law analysis of reacting systems

Exergy destruction

$$\mathcal{X}_{destroyed} = T_0 S_{gen}$$

Reversible work:

It defines the maximum (real or potential) work that can be done during a process.

$$W_{rev} = \sum N_P \left(\bar{h}_f^o + \bar{h} - \bar{h}^o - T_0 \bar{S} \right)_R - \sum N_R \left(\bar{h}_f^o + \bar{h} - \bar{h}^o - T_0 \bar{S} \right)_P$$

Example [Cengel page 726]

Methane (CH_4) gas enters a steady-flow adiabatic combustion chamber at 25°C and 1 atm. It is burned with 50% excess air that also enters at 25°C and 1 atm. Assuming complete combustion and an adiabatic flame temperature of 1789 K, determine the entropy generation.