Reacting Gas Mixtures

Reading	**Problems**
15-1 ⟶ 15-7	15-25, 15-38, 15-62, 15-74, 15-87, 15-93, 15-102, 15-112, 15-113

Definitions

Combustion Process:

- a fuel made up of hydrocarbons is said to have burned completely if:
  - all the carbon present in the fuel is burned to carbon dioxide
  - all the hydrogen is burned to water
- if the conditions are not fulfilled the combustion process is incomplete

Combustion Reactions:

$$\textbf{reactants} \longrightarrow \textbf{products}$$

or

$$\textbf{fuel} + \textbf{oxidizer} \longrightarrow \textbf{products}$$

Fuels:

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
  - liquids ⟶ gasoline - octane, C_8H_{18}
  - gases ⟶ methane, CH_4
  - solids ⟶ coal

Combustion Air:

- oxygen is required in every combustion reaction
- in most combustion reactions air provides the needed oxygen
- dry air is considered to be

$$\left.\begin{matrix}\textbf{21\% oxygen} \\ \textbf{79\% nitrogen}\end{matrix}\right\} \text{on a molar basis}$$

$$molar\ ratio = \frac{n_{N_2}}{n_{O_2}} = \frac{0.79}{0.21} = 3.76$$

$1\ mole$ of air can then be written as $[0.21\ O_2\ +\ 0.79\ N_2]$
For convenience, we typically refer to air as $[O_2\ +\ 3.76\ N_2]$ which is actually 4.76 moles of air.

Air-Fuel Ratio:

$$\frac{mass\ of\ air}{mass\ of\ fuel} = \frac{moles\ of\ air \times \tilde{M}_{air}}{moles\ of\ fuel \times \tilde{M}_{fuel}}$$

$$AF = \bar{AF}\left(\frac{\tilde{M}_{air}}{\tilde{M}_{fuel}}\right)$$

where:

AF - air fuel ratio on a mass basis

$\overline{AF}$ - air fuel ratio on a molar basis

$\tilde{M}_{air}$ = 28.97 kg/kmole

Theoretical or Stoichiometric Air:

- the minimum amount of air that supplies sufficient oxygen for complete combustion of all carbon and hydrogen in the fuel - referred to as stoichiometric, 100% stoichiometric or theoretical
- normally the amount of air supplied is given as a percentage of the theoretical value i.e. 150% = 1.5 × the theoretical air
  - referred to as 50% excess air, 150% stoichiometric

Equivalence Ratio:

- defined as

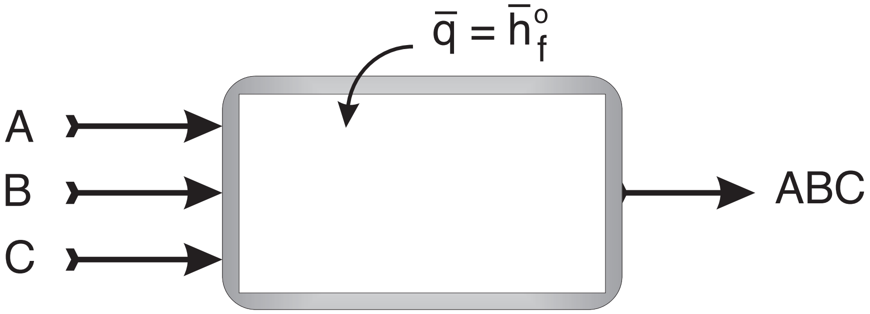
$$equivalence\ ratio = \frac{AF_{actual}}{AF_{theoretical}}$$

- if the equivalence ratio is:
  - > 1 → lean mixture (excess air)
  - < 1 → rich mixture (not enough air)

Conservation of Energy for Reacting Systems

Enthalpy of Formation

- when chemical reactions occur, reactants disappear and products are formed
  → differences cannot be calculated for all substances involved
- it is necessary to establish a common base to account for differences in composition
- $h = 0$ assigned to elements in their most stable form i.e. $O_2, N_2, C, etc.$
- **Enthalpy of Formation:** *the energy released or absorbed when a compound is formed from its stable elements at STP*



where $\overline{h}_f^o$ is the enthalpy of formation.

Taking an energy balance over the combustion chamber shown above, we obtain

$$\underbrace{a\,\overline{h}_A^o + b\,\overline{h}_B^o + c\,\overline{h}_C^o}_{generally=0} + \overline{h}_f^o \longrightarrow \overline{h}_{ABC}^o$$

In general

$$\overline{h}_f^o = \overline{h}_{comp}^o - \sum \overline{n}_i \overline{h}_i^o \quad (kJ/kmole)$$

where
$\overline{n}_i$ = # of moles of i'th elemental substance in forming a single mole of compound (unitless)

Effects of Non-Standard Temperature

$$\overline{h}(T,P) = \overline{h}_f^o + \underbrace{(\overline{h}_{T,P} - \overline{h}^o_{T=25\ ^\circ C,\ P=1\ atm})}_{\Delta\overline{h}\ at\ known\ temperatures}$$

where

$\overline{h}_f^o$	is the heat resulting from a chemical change at $T = 25\ ^\circ C$ and $P = 1\ atm$
$\Delta\overline{h}$	is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $T_{ref} = 25\ ^\circ C$

Effects of Non-Standard Pressure

$$\overline{h}(T,P) = \overline{h}_f^o + \overline{h}_{T,P} - \overline{h}^o_{T=25\ ^\circ C} - P\overline{v}$$

but for an ideal gas

$$P\overline{v} = \mathcal{R}T$$

This allows us to write the pressure in terms of temperature.

$$\overline{h}(T,P) = \overline{h}_f^o + \underbrace{(\overline{h}_{T,P} - \overline{h}^o_{T=25\ ^\circ C} - \mathcal{R}T)}_{\Delta\overline{h}\ at\ known\ temperatures}$$

Enthalpy of Combustion

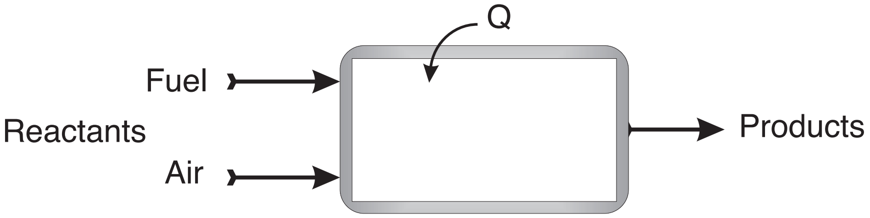
- **Enthalpy of Combustion:** *the difference between the enthalpy of the products and the enthalpy of the reactants where complete combustion occurs at a given temperature and pressure*

$$Q = \sum(mh)_P - \sum(mh)_R = \underbrace{H_P(T_P) - H_R(T_R)}_{H_{RP}}$$

$$Q = \sum(n\overline{h})_P - \sum(n\overline{h})_R = \underbrace{\overline{H}_P(T_P) - \overline{H}_R(T_R)}_{\overline{H}_{RP}}$$

where

$$\overline{h}_c = H_{RP}/kmole\ of\ fuel$$



+ve Q - endothermic
-ve Q - exothermic

Heating Value

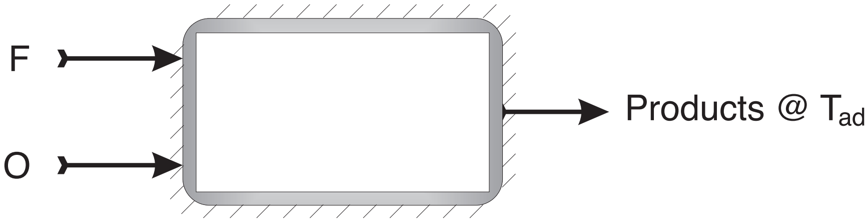
- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion when products are returned to the state of the reactants
- two values are used
  - **HHV**: higher heating value - obtained when all the water formed by combustion is a liquid at the reference temperature
  - **LHV**: lower heating value - obtained when all the water formed by combustion is a vapour as an ideal gas in the mixture of the products
- the HHV exceeds the LHV by the energy required to vaporize the liquid formed

$$
\begin{aligned}
HHV &= LHV + \frac{(m \cdot h_{fg})_{H_2O}}{kmole\ of\ fuel} \\
&= LHV + (\tilde{M} \cdot h_{fg})_{H_2O} \cdot \frac{n_{H_2O}}{n_{fuel}}
\end{aligned}
$$

where

$$
\begin{aligned}
h_{fg}(25\,^\circ C) &= 2,442.3\, kJ/kg \\
\tilde{M}_{H_2O} &= 18.015\, kg/kmole
\end{aligned}
$$

Adiabatic Flame Temperature



- if the system is perfectly insulated it cannot dispose of the LHV and the LHV goes into heating the products above the reference temperature
- under adiabatic conditions, the maximum temperature attained by the products when combustion is complete is called the adiabatic flame or adiabatic combustion temperature

$$H_P(T_{ad}) = H_R(T_R)$$

$$\sum_P n_P\, (\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta\overline{h}})_P = \sum_R n_R\, (\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta\overline{h}})_R$$

We need to collect terms based on what we know or can readily calculate and what we do not know, i.e. terms that are a function of T_{ad}.

$$\sum_P \underbrace{n_P\,(\bar{h})_P}_{\substack{sensible\ heat\\ function\ of\ T_{ad}}} = \sum_R \underbrace{n_R\,(\bar{h}-\bar{h}^o)_R - \left(-\sum_P n_P\,(\bar{h}^o)_P\right)}_{\substack{sensible\ heat\\ function\ of\ T_R\ or\ T_{ref}}}$$

$$+\sum_R \underbrace{n_R\,(\bar{h}^o_f)_R - \sum_P n_P\,(\bar{h}^o_f)_P}_{\substack{chemical\ heat\\ function\ of\ T_R\ or\ T_{ref}}}$$

Step 1: Calculate the right hand side based on known values of T_R and T_{ref}.

Step 2: Calculate the left hand side based on a guessed value of T_{ad}.

Step 3: Repeat Step 2, until LHS = RHS.

Evaluation of Entropy for Reacting Systems

The 2nd law entropy equation can be written as

$$\underbrace{S_{in} - S_{out}}_{due\ to\ heat\ \&\ mass\ transfer} + \underbrace{S_{gen}}_{generation} = \underbrace{\Delta S_{system}}_{change\ in\ entropy}$$

For a closed system, such as a combustion process, the entropy balance on the system can be written as

$$\sum \frac{Q_i}{T_i} + S_{gen} = S_P - S_R$$

- absolute entropy at 1 atm and temperature T is denoted as $s^o(T)$ or $\overline{s}^o(T)$ for a per unit mass or per mole basis
- while $\overline{h}$ was only a function of temperature for ideal gases, we must account for the effects of both T and P in entropy
- the entropy at any value of T and P can be calculated as

$$\overline{s}(T, P) = \underbrace{\overline{s}^o(T)}_{tables} - \mathcal{R} \ln \left(\frac{P_i}{P_{ref}} \right)$$

- the partial pressure P_i can also be written as

$$P_i = Y_i P$$

and

$$\overline{s}(T, P_i) = \overline{s}_i^o(T) - \mathcal{R} \ln \left(\frac{Y_i P}{P_{ref}} \right)$$

where P is the mixture pressure and Y_i is the mole fraction of the $i'th$ component.