Reacting Gas Mixtures

	Reading	**Problems**
	15-1 $\rightarrow$ 15-7	15-21, 15-32, 15-51, 15-61, 15-74
		15-83, 15-91, 15-93, 15-98

Introduction

- thermodynamic analysis of reactive mixtures is primarily an extension of the principles we have learned thus far

- it is necessary to modify the methods used to calculate specific enthalpy, internal energy and entropy

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:

reactants $\rightarrow$ products

or

fuel + oxidizer $\rightarrow$ products

- in all cases the mass is conserved

mass of products = mass of reactants

Fuels:

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
    - liquids $\rightarrow$ gasoline - octane, C_8H_{18}

– gases $\longrightarrow$ methane, CH_4
  – solids $\longrightarrow$ 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

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

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

1 *mole* of air can then be written as $[\textbf{0.21}\ O_2 + \textbf{0.79}\ N_2]$

For convenience, we typically refer to air as $[O_2 + \textbf{3.76}\ N_2]$ which is actually 4.76 moles of air.

Note: From the Amagat model, we know that a mixture at a known T and P (as is the case with combustion reactions)

$$\frac{n_i}{n} = \frac{V_i}{V}$$

Therefore, by expressing a mixture in terms of the number of moles we are also expressing it in terms of a <u>volume fraction</u>.

- nitrogen does not undergo a chemical reaction in combustion since it is inert

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

- no free oxygen would appear in the products

- greater than stoichiometric leads to free oxygen in the products

- less than stoichiometric and C, CO, OH, H_2 will appear in the products since there is not enough oxygen to form water or carbon dioxide (the actual proportions will depend on the temperature and the pressure)

- 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 20% excess air, 120% stoichiometric
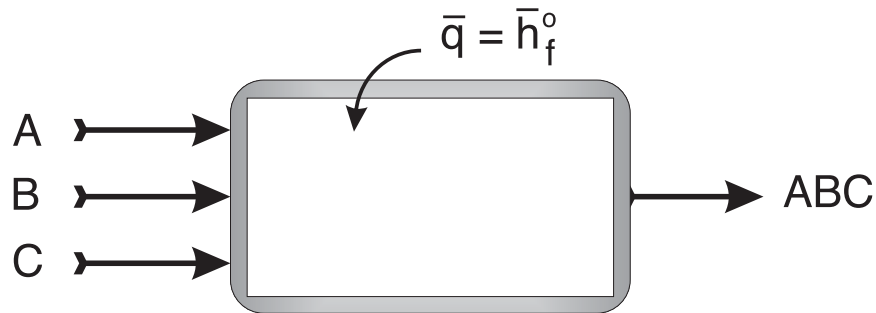
Equivalence Ratio:

- defined as

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

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

Conservation of Energy for Reacting Systems

Enthalpy of Formation

- previous calculations involving enthalpy were all based on differences and the reference used to determine enthalpy did not matter

- when chemical reactions occur, reactants disappear and products are formed
  $\rightarrow$ differences cannot be calculated for all substances involved

- it is necessary to establish a common base to account for differences in composition

- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure

  - $T_{ref} = 25°C \rightarrow 298\ K$
  - $P_{ref} = 1\ atm$

- $h = 0$ 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

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

The left side of the equation is typically zero because $h = 0$ for elements in their stable form. The sign of $\overline{h}_f^o$ indicates the direction of heat flow; +ve is endothermic and -ve is exothermic.

Effects of Non-Standard Temperature

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

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, $T_{ref} = 25\ ^\circ C$
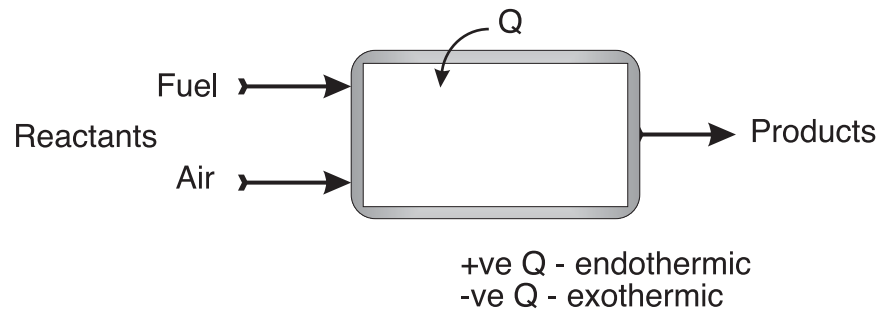
Enthalpy of Combustion

- while the enthalpy of formation is related to elemental reactants $\longrightarrow$ resulting in a single compound; the **enthalpy of combustion** is related to $fuel + oxidizer$ as the reactants

- **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

with:

$$+ve\ Q \;\Rightarrow\; endothermic$$

$$-ve\ Q \;\Rightarrow\; exothermic$$

- when enthalpy of formation data are available for all products and reactants the above equation can be used

- otherwise a calorimeter must be used to measure the enthalpy of combustion

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

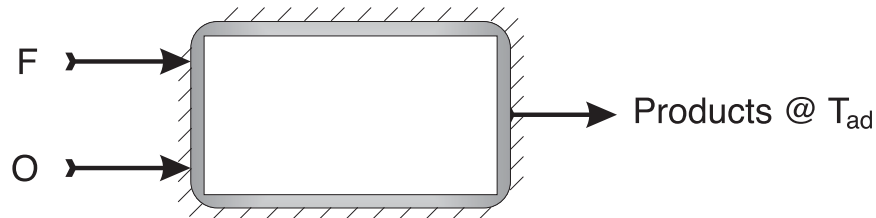- the HHV exceeds the LHV by the energy required to vaporize the liquid formed

$$HHV \;=\; LHV + \frac{(m \,\cdot\, h_{fg})_{H_2O}}{kmole \; of \; fuel}$$

$$=\; LHV + (\tilde{M} \,\cdot\, h_{fg})_{H_2O} \,\cdot\, \frac{n_{H_2O}}{n_{fuel}}$$

where

$$h_{fg}(25\,°C) \;=\; 2,442.3 \; kJ/kg$$

$$\tilde{M}_{H_2O} \;=\; 18.015 \; kg/kmole$$

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}.

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

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

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.

Dew Point

- since water is formed when hydrocarbon fuels are burned, the mole fraction of water vapour in the form of gaseous products can be significant

- if the gaseous products of combustion are cooled at constant mixture pressure the dew point temperature is reached when water vapour begins to condense

- since corrosion of duct work, mufflers etc. can occur, the knowledge of dew point temperature is important

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

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

- a common datum must be used to assign entropy values for each substance involved in the reaction

- an entropy of 0 for pure crystalline substances is obtained at absolute zero

- the entropy relative to this datum is called absolute entropy

- 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

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

where

$$
\begin{aligned}
P_{ref} &= 1 \, atm \\
P_i &= partial \, pressure \, of \, i'th \, component \\
\mathcal{R} &= 8.31434 \, kJ/kmole \cdot K
\end{aligned}
$$

- 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.