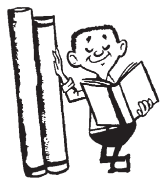
# *Reacting Gas Mixtures*



| Reading | Problems |
|---|---|
| 14-1 $\longrightarrow$ 14-7 | 14-16, 14-22, 14-42, 14-48, 14-68, 14-77, 14-91, 14-93 |

## 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:***

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

or

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

- in all cases the mass is conserved

  $$\textbf{mass of products} = \textbf{mass of reactants}$$

***Fuels:***

- fuel is simply a combustible substance
- hydrocarbon fuels exist as liquids, gases and solids
  - liquids $\longrightarrow$ 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

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

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

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

**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 volume fraction.

- 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 $\times$ the theoretical air
  - referred to as 20% excess air, 120% stoichiometric

***Equivalence Ratio:***

- defined as

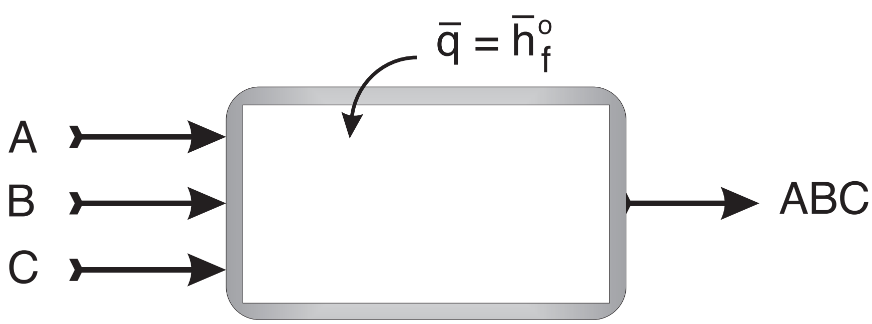
$$equivalence\ ratio = \frac{AF_{actual}}{AF_{theoretical}}$$

- if the equivalence ratio is:
  - $> 1$ $\longrightarrow$ lean mixture (excess air)
  - $< 1$ $\longrightarrow$ 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
  $\longrightarrow$ 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

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

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

# Enthalpy of Combustion

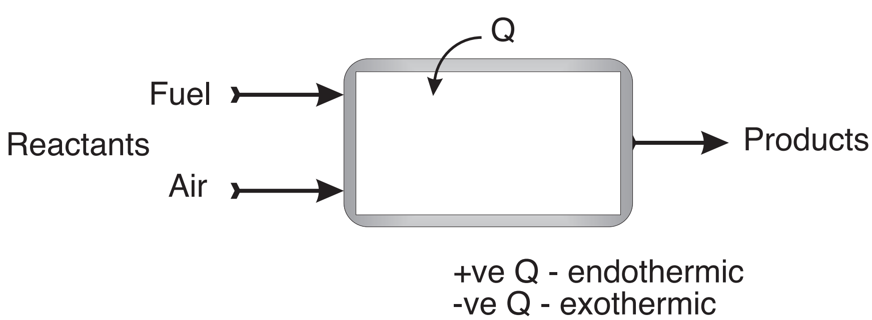
- while the enthalpy of formation is related to elemental reactants $\longrightarrow$ resulting in a single compound; the **enthalpy of combustion** is related to $fuel + oxidizer$ as the reactants
- **Enthalpy of Combustion:** *the difference between the enthalpy of the products and the enthalpy of 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

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




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

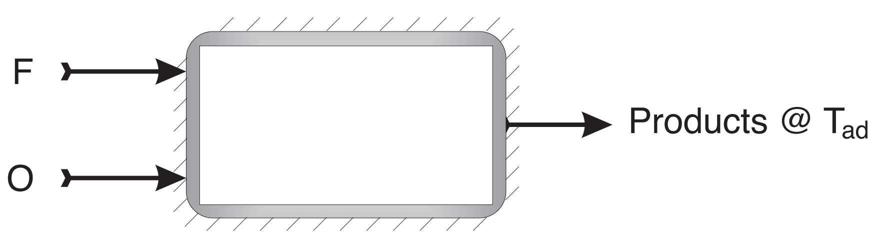
- the heating value of a fuel is a positive value equal to the magnitude of the enthalpy of combustion when products are returned to the state of the reactants
- two values are used
  - **HHV**: higher heating value - obtained when all the water formed by combustion is a liquid at the reference temperature
  - **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

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

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 $T_{ad}$.

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

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

**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.