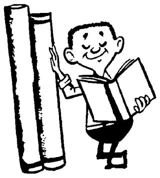
Reacting Gas Mixtures



Reading	Problems
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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 → products

or

fuel + oxidizer → 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 → gasoline - octane, C_8H_{18}
  - gases → methane, CH_4
  - solids → coal

Combustion Air:

- 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 $[0.21\ O_2\ +\ 0.79\ N_2]$

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

Equivalence Ratio:

- defined as

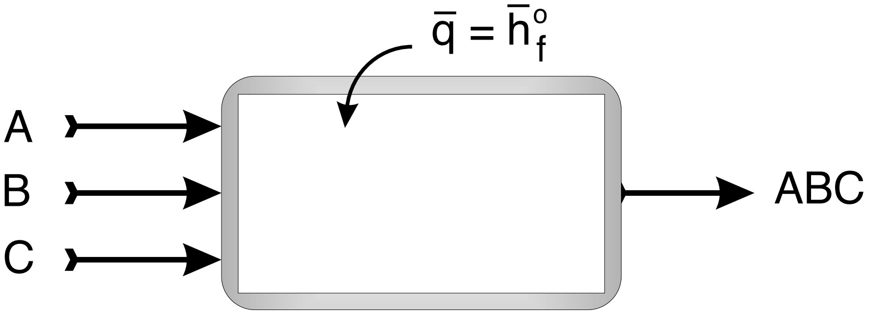
$$equivalence\ ratio = \frac{AF_{actual}}{AF_{theoretical}}$$

- 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
- the enthalpy datum for reacting systems is set to zero at standard temperature and pressure
  - $\boldsymbol{T_{ref} = 25°C \rightarrow 298\ K}$
  - $\boldsymbol{P_{ref} = 1\ atm}$
- $\boldsymbol{h = 0}$ assigned to elements in their most stable form i.e. $\boldsymbol{O_2, N_2, C, etc.}$
- **Enthalpy of Formation:** *the energy released or absorbed when a compound is formed from its stable elements at STP*



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

Effects of Non-Standard Temperature

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

where

$\boldsymbol{\overline{h}_f^o}$ is the heat resulting from a chemical change at $\boldsymbol{T = 25\ °C}$ and $\boldsymbol{P = 1\ atm}$

$\boldsymbol{\Delta\overline{h}}$ is the heat resulting from a change in temperature (sensible heat) with respect to the reference temperature, $\boldsymbol{T_{ref} = 25\ °C}$

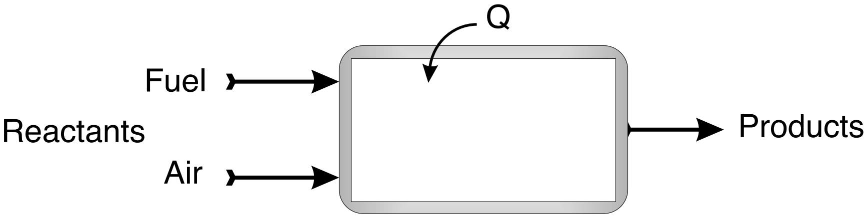
Enthalpy of Combustion

- **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*

$$\begin{aligned} Q &= \sum(mh)_P - \sum(mh)_R = \underbrace{H_P(T_P) - H_R(T_R)}_{H_{RP}} \\ Q &= \sum(n\overline{h})_P - \sum(n\overline{h})_R = \underbrace{\overline{H}_P(T_P) - \overline{H}_R(T_R)}_{\overline{H}_{RP}} \end{aligned}$$

where

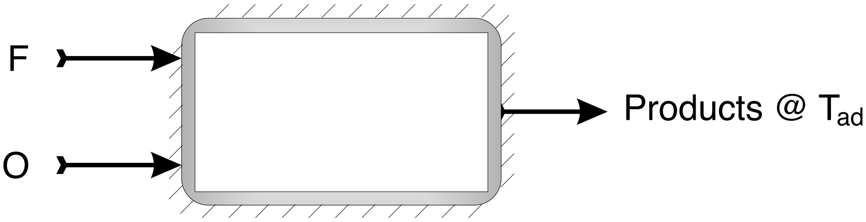
$$\overline{h}_c = H_{RP}/kmole\ of\ fuel$$



+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 <u>liquid</u> at the reference temperature
  - **LHV**: lower heating value - obtained when all the water formed by combustion is a <u>vapour</u> as an ideal gas in the mixture of the products



Adiabatic Flame 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}.

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

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

Fuel	**Oxidizer** **Oxygen** (K)	 **Air** (K)
H_2	3079	2384
CH_4 (methane)	3054	2227
C_3H_8 (propane)	3095	2268
C_8H_{18} (octane)	3108	2277

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

Example:

The pressure of the water vapour is given as

$$\boldsymbol{P_w = X_w\ P}$$

where the mole fraction is

$$\boldsymbol{X_w = \frac{n_w}{n}}$$

As an example

$$\boldsymbol{CH_4 + 2(O_2 + 3.76N_2) \longrightarrow 1\ CO_2 + 2\ H_2O + 7.52\ N_2}$$

$$\boldsymbol{X_w = \frac{c}{b+c+d} = \frac{2}{10.52} = 0.190}$$

Knowing that the overall pressure of the products is $\boldsymbol{1\ atm}$, we can find $\boldsymbol{P_w}$ as

$$\boldsymbol{P_w = X_w\ P = 0.190\ \times\ 1\ atm = 0.190\ atm}$$

From the saturate water tables, we can find the temperature that corresponds to a vapour pressure of $\boldsymbol{0.190\ atm}$ or $\boldsymbol{19.25\ kPa}$.

The dew point temperature is approximately $\boldsymbol{T_{DP} \approx 60\ ^\circ C}$.

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

  $$P_i = X_i P$$

  and

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

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