# **Reacting Gas Mixtures**



## 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:**

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reactants \rightarrow products
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or

 $fuel + oxidizer \rightarrow products$ 

• in all cases the mass is conserved mass of products = mass of reactants

#### Fuels:

- hydrocarbon fuels exist as liquids, gases and solids
  - liquids  $\rightarrow$  gasoline octane,  $C_8H_{18}$
  - gases  $\rightarrow$  methane,  $CH_4$
  - solids  $\rightarrow$  coal

#### Combustion Air:

• oxygen is required in every combustion reaction

• dry air is considered to be

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

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

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:

 $egin{aligned} rac{mass \ of \ air}{mass \ of \ fuel} &= rac{moles \ of \ air imes ilde{M}_{air}}{moles \ of \ fuel imes ilde{M}_{fuel}} \ AF &= ar{AF}\left(rac{ ilde{M}_{air}}{ ilde{M}_{fuel}}
ight) \end{aligned}$ 

where:

*AF* - air fuel ratio on a mass basis

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

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

#### 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

#### Equivalence Ratio:

• defined as

$$\Phi = \frac{FA_{actual}}{FA_{theoretical}} = \frac{AF_{theoretical}}{AF_{actual}}$$
$$= \frac{\frac{\text{mass of air theoretical}}{\frac{\text{mass of fuel}}{\text{mass of air actual}}}{\frac{\text{mass of fuel}}{\text{mass of fuel}}}$$

 $= \frac{\text{mass of air theoretical}}{\text{mass of air actual}}$ 

• 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**

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

$$\underbrace{a \ \overline{h}^o_A + b \ \overline{h}^o_B + c \ \overline{h}^o_C}_{generally=0} + \overline{h}^o_f \ \longrightarrow \ \overline{h}^o_{ABC}$$

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.

In general

$$\overline{h}^{o}_{f} = \overline{h}^{o}_{comp} - \sum \overline{n}_{i}\overline{h}^{o}_{i} ~~(kJ/kmol)$$

where

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

### **Effects of Non-Standard Temperature**

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

where

- $\overline{h}^o_f$  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**

$$\overline{h}(T,P) = \overline{h}^o_f + \overline{h}_{T,P} - \overline{h}^o_{T=25\ ^oC} - P\overline{v}$$

but for an ideal gas

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

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

$$\overline{h}(T,P) = \overline{h}_{f}^{o} + \underbrace{(\overline{h}_{T,P} - \overline{h}_{T=25\ ^{o}C}^{o} - \mathcal{R}T)}_{\downarrow \overline{\downarrow} \ \overline{\downarrow}$$

 $\Delta \overline{h}$  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

 $\overline{h}_{c} = H_{RP}/kmol \ of \ fuel$ 



with:

 $+ve Q \Rightarrow endothermic$  $-ve Q \Rightarrow exothermic$ 

# **Heating Value**

- 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
- Table 15.3 lists HHV and LHV for commonly used fuels

$$egin{aligned} HHV &= LHV - rac{m_{H_2O}}{m_{fuel}} \cdot (h_{fg})_{H_2O} \ &= LHV - \cdot rac{(n \cdot ilde{M})_{H_2O}}{(n \cdot ilde{M})_{fuel}} \cdot (h_{fg})_{H_2O} \end{aligned}$$

where

$$egin{array}{rcl} h_{fg}(25\ ^{\circ}C) &=& 2,442.3\ kJ/kg \ && ilde{M}_{H_{2}O} &=& 18.015\ kg/kmol \end{array}$$

# **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

$$\begin{split} H_P(T_{ad}) &= H_R(T_R) \\ \sum_P n_P \; (\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta \overline{h}})_P &= \sum_R n_R \; (\overline{h}_f^o + \underbrace{\overline{h} - \overline{h}^0}_{\Delta \overline{h}})_R \end{split}$$

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  $T_{ad}$ .

$$\sum_{P} \underbrace{\underbrace{n_{P}(\bar{h})_{P}}_{sensible \ heat}}_{function \ of \ T_{ad}} = \sum_{R} \underbrace{n_{R}(\bar{h} - \bar{h}^{o})_{R} - \left(-\sum_{P} n_{P}(\bar{h}^{o})_{P}\right)}_{sensible \ heat}}_{function \ of \ T_{R} \ or \ T_{ref}} + \sum_{R} \underbrace{n_{R}(\bar{h}^{o}_{f})_{R} - \sum_{P} n_{P}(\bar{h}^{o}_{f})_{P}}_{chemical \ heat}}_{function \ of \ T_{R} \ or \ T_{ref}}$$

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

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

- 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

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

where

$$P_{ref} = 1 atm$$
  
 $P_i = partial \ pressure \ of \ i'th \ component$   
 $\mathcal{R} = 8.31451 \ kJ/kmol \cdot K$ 

• the partial pressure  $P_i$  can also be written as

$$P_i = Y_i P$$

and

$$\overline{s}(T,P_i) = \overline{s}^o_i(T) - \mathcal{R} \ln \left(rac{Y_i P}{P_{ref}}
ight)$$

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

#### **PROBLEM STATEMENT:**

Liquid octane  $(C_8H_{18})$  enters a steady-flow combustion chamber at 25 °C and 1 *atm* at a rate of 0.4 kg/min. It is burned with 50% excess air that also enters at 25 °C. If it is assumed that  $T_0 = 298 \ K$ , the products leave the combustion chamber at 1 *atm*, the combustion process is complete and that all the  $H_2O$  in the products is in liquid form. Determine the entropy generation rate  $[kJ/(min \cdot K)]$  and the irreversibility [kW]