7. Chemical Reactions

Substance: Nucleus, orbiting electrons, atoms, molecules

Pure Substance: Chemical purity

Chemical Reaction: Re-arrangement of electrons and re-grouping of atoms to form new molecules

Burning: Type of chemical reaction, usually involving oyygen

Combination with oxygen

Combustion: Violant burning (usually of hydrocarbons)

Hydrocarbons: (chemical) molecules made up of basically C and H ; made in living plants

Combustion of Hydrocarbons: is important because they are the primary energy sources (nuclear and hydro not included)

7.1 Hydrocarbon Fuels

Coal, Gasoline, Diesel oil, Natural gas, Kerosene, others

Coal: Vegetation deposits of past geological ages

Made up of C, H_2, O_2, S, N_2, moisture, others

Coal analysis:

Ultimate analysis:

Gives percent of constituents by mass of unburned coal

- As received basis
- Dry basis
- Ash-free basis

Or combination

Proximate analysis:

Gives percent (by mass) of volatile matter, fixed carbon, ash, and moisture of unburned coal

Orsat analysis:

Gives percent (by volume) of CO, CO_2, and O_2 content of product gases of combustion

Other Coal Properties: Grindability, Size, Fusibility of ash, others

Coal Classification - Antricite (~ 80 % carbon)
- Bituminous (~ 60 % carbon)
- Lignite (~ 40 % carbon)

Crude oil: Distillation and cracking yields most liquid hydrocarbon fuels all containing large number of various hydrocarbons (Gasoline has 40 kinds, for instance)

Gasoline: Mostly C_8H_{18} - Octane

Diesel Oil: Mostly $C_{12}H_{26}$ – Dodecane (fuel oil)

Gaseous Fuels: Natural gas – mostly CH_4 methane

(93 % CH_4, 3 % C_2H_6, 3 % N_2)

Gaseous Artificial Fuels: Coal gas, Producer gas, Blast furnace gas, etc.

7.2 Combustion Process

$$\left.\underbrace{\begin{array}{ccc} C & + & O_2 \\ 1\text{ mole} & & 1\text{ mole} \\ 12\text{ kg} & & 32\text{ kg} \end{array}}_{\text{Reactants}} \rightarrow \underbrace{\begin{array}{c} CO_2 \\ 1\text{ mole} \\ 44\text{ kg} \end{array}}_{\text{Product}} \right\}$$

Note that 12, 32, and 44 are approximate molecular weights

STP – Standard Temperature and Pressure – 0 °C and 100 kPa

$$\left.\underbrace{CH_4 \quad + \quad 2\,O_2}_{\text{Gas at STP}} \quad \rightarrow \quad \underbrace{CO_2}_{\text{Gas at STP}} \quad + \quad \underbrace{2\,H_2O}_{\text{Liquid at STP}}\right\}$$

State of the products depends on temperature, pressure, etc

Oxygen is supplied in Air: 21 % Oxygen and 79 % Nitrogen

moleular weight = 32 approximately

In the air, for each mole of Oxygen, there is 21/79 = 3.76 moles of Nitrogen

$$CH_4 \quad + \quad \underbrace{2\,O_2 \quad + \quad 2\,(3.76)\,N_2}_{\text{Air}} \quad \rightarrow \quad CO_2 \quad + \quad 2\,H_2O \quad + \quad 7.52\,N_2$$

Theoretical air: Minimum amount of air, on molal basis, necessary for complete combustion

Complete combustion: $C \rightarrow CO_2$ $S \rightarrow SO_2$ $H \rightarrow H_2O$

Assuming that Nitrogen is not burning (requires high pressure and high temperature)

Excess air: Amount of air, usually by mole, supplied in excess of theoretical air

$$\text{Air-Fuel ratio} = \frac{\text{Mass of air}}{\text{Mass of Fuel}}$$

sometimes on molal basis

Example: Incomplete combustion of methane with 10 % CO in the products (molal basis) and theoretical air.

$$CH_4 + \underbrace{2\,O_2 + 7.52\,N_2}_{\text{Theoretical Air}} \rightarrow 0.9\,CO_2 + 0.1\,CO + 2\,H_2O + 0.05\,O_2 + 7.52\,N_2$$

Example: Fuel oil ($C_{12}H_{26}$) is burned with 50 % excess air (molal basis). Find the volumetric percent of the products

$$C_{12}H_{26} + 1.5\,[18.5\,O_2 + (18.5)\,(7.52)\,N_2] \rightarrow 12\,CO_2 + 13\,H_2O + 9.25\,O_2 + 104.3\,N_2$$

Total moles of the products = 12 + 13 + 9.25 + 104.3 = 138.55

$$CO_2 \quad \frac{12}{138.55} = 0.0866 \quad \Rightarrow \quad 8.66\ \%\ CO_2 \ \text{ by mole (or volume)}$$

$$H_2O \quad \frac{13}{138.55} = 0.0938 \quad \Rightarrow \quad 9.38\ \%\ H_2O$$

$$O_2 \quad \frac{9.25}{138.55} = 0.0668 \quad \Rightarrow \quad 6.68\ \%\ O_2$$

$$N_2 \quad \frac{104.3}{138.55} = 0.7528 \quad \Rightarrow \quad 75.28\ \%\ N_2$$

100 % products

Example: Ultimate analyis of coal: 74 % C, 5 % H_2, 6 % O_2, 1 % S, 1.2 % N_2, 3.8 % moisture, 9 % Ash. Find the theoretical air-fuel ratio (AF) in kg air / kg fuel. Assume complete burning.

$C + O_2 \rightarrow CO_2 \quad \Rightarrow$ 12 kg of C requires 32 kg of O_2 for complete burning

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Rightarrow$ 2 kg of H requires 16 kg of O_2 for complete burning

$S + O_2 \rightarrow SO_2 \quad \Rightarrow$ 32 kg of S requires 32 kg of O_2 for complete burning

$$\left(\frac{32}{12}\ \frac{\text{kg } O_2}{\text{kg C}}\right)\left((0.74)\left(\frac{\text{kg C}}{\text{kg fuel}}\right)\right) + \left(\frac{16}{2}\right)(0.05) + \left(\frac{32}{32}\right)(0.01) = 2.3833\ \frac{\text{kg } O_2}{\text{kg fuel}}$$

Air has 23 % by mass O_2 or $0.23\ \frac{\text{kg } O_2}{\text{kg air}}$

$$AF = \frac{0.3833}{0.23}\ \frac{\text{kg } O_2 / \text{kg fuel}}{\text{kg } O_2\ / \text{kg air}} = 10.36\ \frac{\text{kg air}}{\text{kg fuel}}$$

7.3 Enthalpy of Formation

Assumption: The enthalpy of all elements is taken to be zero at the arbitrary reference state of 25 °C and 100 kPa.

$$C + O_2 \rightarrow CO_2$$

H_R at ref. state H_P at ref. state

H_R: Enthalpy of reactants

H_P: Enthalpy of products

Thermal energy released:

$$Q = H_P - H_R$$

$$Q = H_P - H_R = \sum_{products} n_i \bar{h}_i - \sum_{reactants} n_j \bar{h}_j$$

$\bar{h}$: molal enthalpy in kJ/kmol of mixture

$\bar{h}_i$: partial molal enthalpy in kJ/kmol of i

For the above reaction:

$$\sum n_i \bar{h}_i = \bar{h}_C + \bar{h}_{O_2} = 0$$

$$\sum n_j \bar{h}_j = \bar{h}_{CO_2}$$

$$Q = -\bar{h}_{CO_2}$$

$$\bar{h}_{CO_2} = -393\,757 \text{ kJ/kmol of } CO_2$$

Enthalpy of formation of CO_2 at the reference state 25 °C and 1 atm.

Enthalpy of formation of compounds are given in thermodynamic tables.

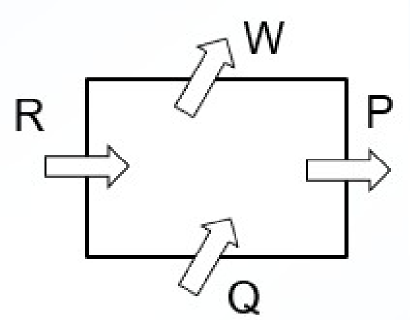
CO_2: - 393 797 kJ/kmol CO: - 110 596 kJ/kmol

H_20 (liq.): - 286 010 kJ/kmol H_20 (gas): - 241 971 kJ/kmol

CH_4: - 74 917 kJ/kg

Sometimes, the reference state is given at 100 kPa instead of 1 atm. This changes the enthalpy values, slightly.

7.4 First Law Analysis of Reacting Systems



$$\dot{Q} + \sum_{R} n_i \, \bar{h}_i \rightarrow \dot{W} + \sum_{P} n_j \, \bar{h}_j$$

n_i: Moles of reactant i

n_j: Moles of product j

h: Entahlpy of formation at the given state

Example: Propane burns in atmospheric air (Steady State Steady Flow – SSSF – process). Both the reactants and the products are at 25 °C and 1 atm. Apply the first law.

$$\underbrace{C_3H_8 + 5\,O_2 + (5)\,(3.76)\,N_2}_{\text{At } 25\,^\circ\text{C and 1 atm}} \rightarrow \underbrace{3\,CO_2 + 4\,H_2O + 18.8\,N_2}_{\substack{\text{At } 25\,^\circ\text{C and 1 atm} \\ H_2O \text{ is in liquid form}}}$$

First law: $\dot{Q} + \sum_R n_i\,\bar{h}_i \rightarrow \dot{W} + \sum_P n_j\,\bar{h}_j \qquad \dot{W} = 0$

$$\sum_R n_i\,\bar{h}_i = \left(\bar{h}_f^0\right)_{C_3H_8} = -\,103\,909 \text{ kJ/kmol}$$

Oxygen and nitrogen are pure gases. So, their enthalpies of formation are zero.

$$\sum_{P} n_j \, \bar{h}_j = 3 \left(\bar{h}_f^0\right)_{CO_2} + 4 \left(\bar{h}_f^0\right)_{\substack{H_2O \\ Liq}} = (3)\,(-\,393\,757) + (4)\,(-\,286\,010)$$

$$= -\,2\,325\,311 \text{ kJ}$$

$$\dot{Q} = -\,2\,325\,311 + 103\,909 = -\,2\,221\,402 \text{ kJ/kmol } C_3H_8$$

Change this to kg basis. Molecular weight of C_3H_8 is 44 kg/kmol

$$\dot{Q} = -\,50\,486.4 \text{ kJ/kg } C_3H_8$$

In most cases, neither the reactants nor the products are at the reference state of 1 atm and 25 °C. Then, we need a correction for the enthalpy of formations.

$$\dot{Q} + \sum_{R} n_i \left[\bar{h}_f^0 + \Delta\bar{h}\right]_i \rightarrow \dot{W} + \sum_{P} n_j \left[\bar{h}_f^0 + \Delta\bar{h}\right]_j$$

The corrections Δh are given in tables.

Example

Diesel engine uses $C_{12}H_{26}$ (dodecane). Air fuel mixture is 200 % theoretical, at 25 °C and 1 atm. $C_{12}H_{26}$ has an enthalpy of foramtion of - 394 199 kJ/kg. After complete combustion, products leaves at 1 atm and 600 K. Heat loss is measured as 232 000 kJ/kmol fuel. Find W in kW if m_f = 1 kmol/hour

$$C_{12}H_{26} + 2\left[18.5\ O_2 + (18.5)(3.76)\ N_2\right] \rightarrow 12\ CO_2 + 13\ H_2O + 18.5\ O2 + 139.12\ N_2$$

First law $$\dot{Q} + \sum_R n_i \left[\bar{h}_f^0 + \Delta\bar{h}\right]_i \rightarrow \dot{W} + \sum_P n_j \left[\bar{h}_f^0 + \Delta\bar{h}\right]_j$$

$$\dot{Q} = -\ 232\ 000\ \text{kJ/kmol fuel}$$

$$\sum_R n_i \left[\bar{h}_f^0 + \Delta\bar{h}\right]_i = \left(\bar{h}_f^0\right)_{C_{12}H_{26}} = -\ 394\ 971\ \text{kJ/kmol fuel}$$

$$\sum_{P} n_j \left[\overline{h}_f^0 + \Delta\overline{h}\right]_j = (12)\ (-\,393\,757 + 12\,916) +$$

$$(13)\ (-\,2412\,971 + 10\,498) +$$

$$(18.5)\ (-\,9\,247) + (139.12)\ (8\,891)$$

$$= -\,6\,171\,255 \text{ kJ(kmol fuel}$$

$$\dot{Q} + H_R = W + H_P \quad => \quad -\,232\,000 - 394\,971 = W - 6\,171\,255$$

$$W = 5\,544\,284 \text{ kJ/kmol fuel}$$

$$\dot{W} = W\,\dot{m}_f = 5\,544\,284 \text{ kJ/hour}$$

$$= 1540 \text{ kJ/s} = 1540 \text{ kW}$$

7.3 Adiabatic Flame Temperature

It is the temperature of the products under the following conditions:

- No work, No heat transfer
- All the available chemical energy is converted to thermal energy and kept in the system
- 100 % theoret,cal air is supplied
- Complete combustion
- No dissociation of products

Example: Propane is burning at 25 °C and 1 atm. Find the adiabatic flame temperature.

$$C_3H_8 + 5\left[O_2 + 3.76\ N_2\right] \rightarrow 3\ CO_2 + 4\ H_2O + 18.8\ N_2$$

$$H_R = \sum_R n_i \left[\bar{h}_f^0 + \Delta \bar{h}_0 \right]_i = (1)\,(-\,103\;909) + 0 + 0$$

$$= -\,103\;909 \text{ kJ7 kmol } C_3H_8$$

$$H_P = (3)\,(-\,393\;757 + \Delta h_{CO_2}) + (4)\,(-\,241\;971 + \Delta h_{H_2O}) +$$

$$(18)\,(0 + \Delta h_{N_2})$$

All the Δh's depend on temperature

Guess 1: $T_1 = 2500$ K => $H_{P1} = 10\;845$ kJ7kmol C_3H_8

Guess 2: $T_2 = 2300$ K => $H_{P2} = -\,206\;068$ kJ7kmol C_3H_8

Using linear interpolation:

$$T = T_1 + \frac{H_R - H_{P_1}}{H_{P_2} - H_{P_1}} \left(T_2 - T_1\right) = 2394 \text{ K} \quad \Rightarrow \quad H_P \cong H_R$$

Adiabatic flame temperature: