PS41 Propulsion – Chapter 2
Chemical Reactions

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Objectives

- Give an overview of fuels and combustion.

- Define the parameters used in combustion analysis, such as air-fuel ratio, percent theoretical air.

- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.

- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.

- Determine the adiabatic flame temperature for reacting mixtures.

- Develop the equilibrium criterion for reacting systems.
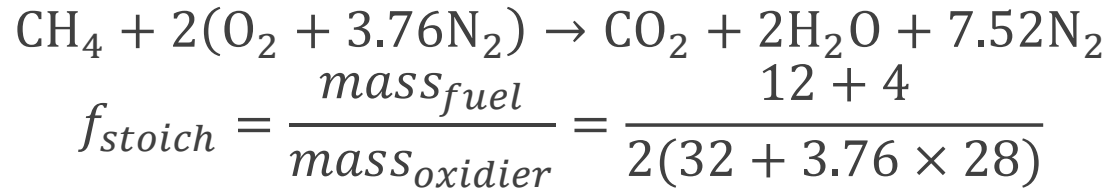
Fuels and Combustion

- Fuel: any material that can be burned to release thermal energy.

- Hydrocarbon fuels: $C_n H_m$

- Combustion: A chemical reaction during which a fuel is oxidized and a large quantity of energy is released.

- $1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air}$

- Conservation of mass principle (the mass balance)

- Air-fuel ratio: $AF = \dfrac{m_{air}}{m_{fuel}}, f = \dfrac{m_{fuel}}{m_{air}}$
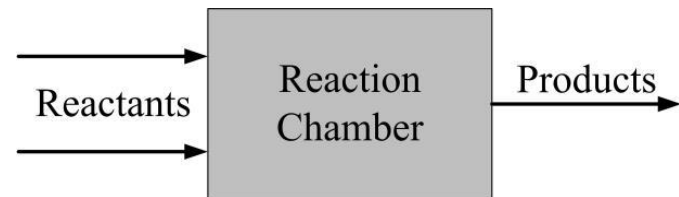
Theoretical and Actual Combustion

- Stoichiometric or theoretical combustion

$$\text{CH}_4 + 2(\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2$$

$$f_{stoich} = \frac{mass_{fuel}}{mass_{oxidier}} = \frac{12 + 4}{2(32 + 3.76 \times 28)}$$

- $\phi = \dfrac{f}{f_{stoich}}$

- $\begin{cases} \phi > 1, rich\ of\ fuel, deficiency\ of\ air \\ \phi = 1, stoichiometric\ ratio \\ \phi < 1, poor\ of\ fuel, excess\ air \end{cases}$

First-Law Analysis of Reacting Systems

- The energy balance (the First-Law) relations are applicable to both reacting and nonreacting systems.
  - $Q = U_2 - U_1 + W_u + W, \delta Q = dU + \delta W_u + \delta W$
  - $Q = U_2 - U_1 + W_{u,V}, \delta Q = dU + \delta W_{u,V}$ （定温等容）
  - $Q = U_2 - U_1 + W_{u,P} + P(V_2 - V_1) = H_2 - H_1 + W_{u,P}, \delta Q = dH + \delta W_{u,P}$ （定温等压）

- $Q_v = U_2 - U_1, \boxed{Q_P = H_2 - H_1}$

- Enthalpy of reaction Δh_R （反应焓）: the difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction.

- Standard reference state:1 atm, 298.15K (25ºC)
  - Property values at the standard reference state are indicated by a superscript (º)

Enthaply of Formation & Enthalpy of Combustion

- For combustion processes, the enthalpy of reaction is usually referred to as the enthalpy of combustion Δh_c（燃烧焓）, which represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure.

$$\Delta h_R = \Delta h_c = H_{prod} - H_{react}$$

- Enthalpy of formation $\Delta \overline{h_f}$（生成焓）: the enthalpy of a substance at a specified state due to its chemical composition.
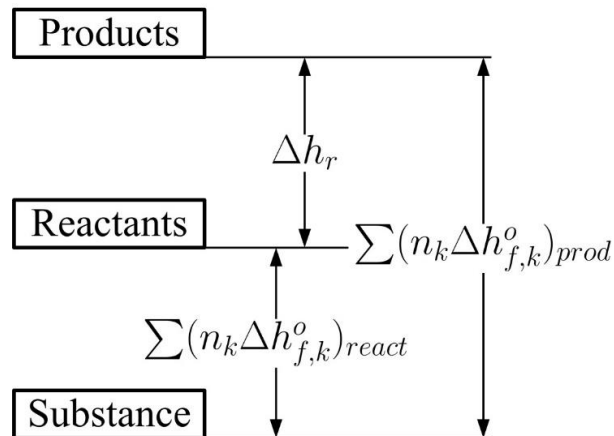
Relationship between Enthalpy of reaction and Enthalpy of formation

Hess's law

■ The change of enthalpy in a chemical reaction (i.e. the heat of reaction at constant pressure) is independent of the pathway between the initial and final states.
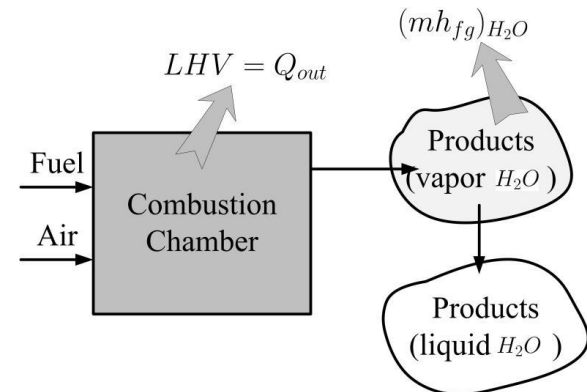
$$\Delta H^{\theta} = \sum \left(\Delta H^{\theta}_{f\ products} \right) - \sum \left(\Delta H^{\theta}_{f\ reactants} \right)$$
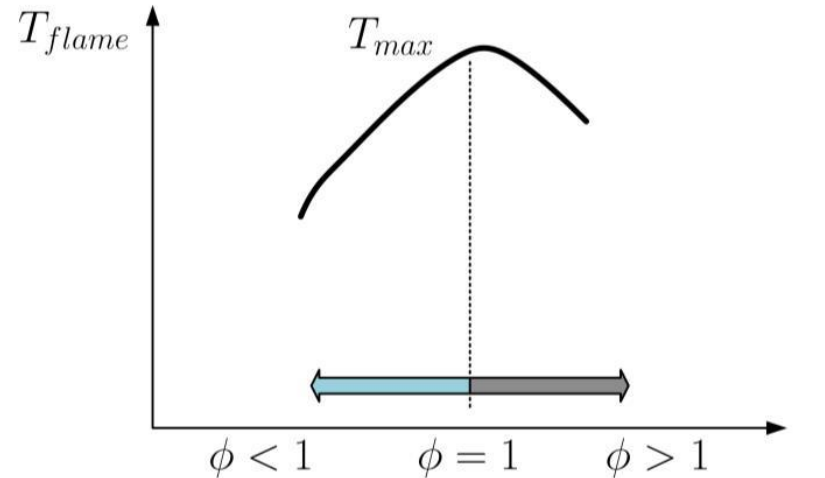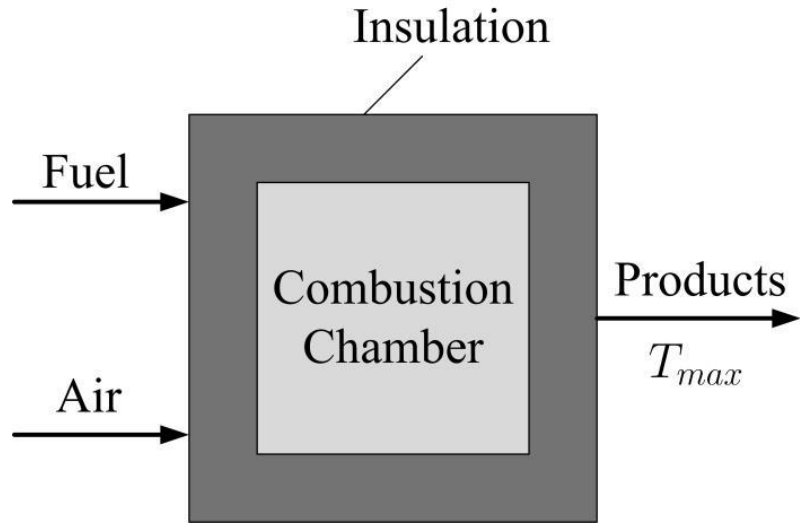
Example 1

Heating Value (1)

■ Heating value of the fuel: the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants.

■ The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

◦ The heating value depends on the phase of the H_2O in the products.

◦ Higher heating value (HHV) when the H_2O in the products is in the liquid form.

◦ Lower heating value (LHV) when the H_2O in the products is in the vapor form.

The higher heating value of a fuel is equal to the sum of the lower heating value of the fuel and the latent heat of vaporization of the H_2O in the products.

$(mh_{fg})_{H_2O}$

$LHV = Q_{out}$

Fuel

Air

Combustion Chamber

Products (vapor H_2O)

Products (liquid H_2O)

Adiabatic Flame Temperature (1)

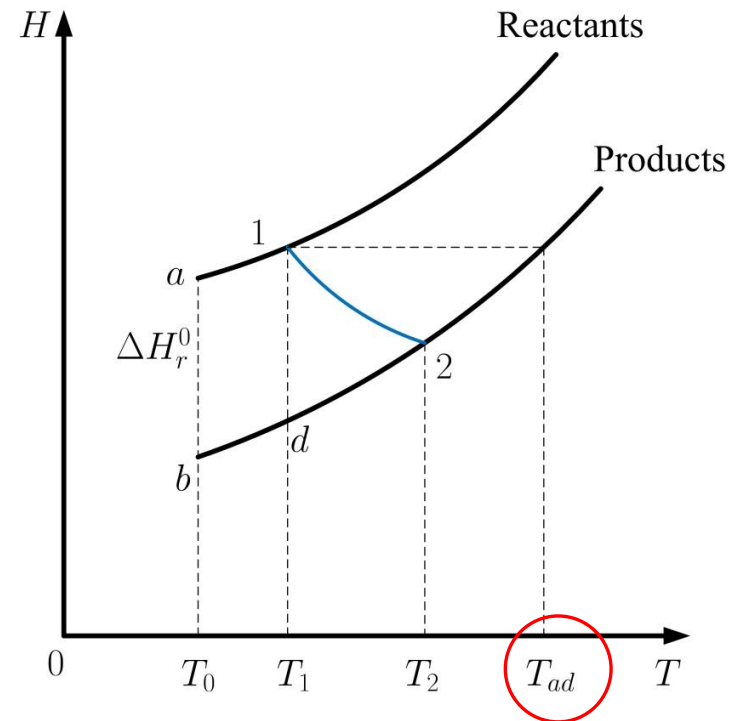
The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings (Q=0)

$$H_{prod} = H_{react}$$

Adiabatic Flame Temperature (2)

- $H_{ad} - H_1 = (H_{ad} - H_b) + \Delta H_r^0 - (H_1 - H_a) = 0$
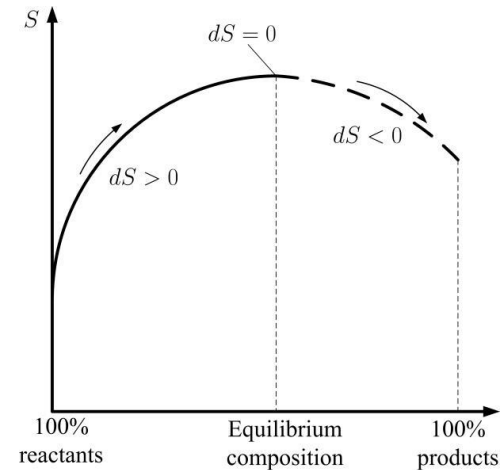- $-\Delta H_r^0 = (H_{ad} - H_b) - (H_1 - H_a)$

Example 2

Chemical and Phase Equilibrium

■ Combining the first- and the second-law relations for this system:

$$\left.\begin{array}{c} \delta Q - PdV = dU \\ dS \geq \dfrac{\delta Q}{T} \end{array}\right\} \; dU + PdV - TdS \leq 0$$
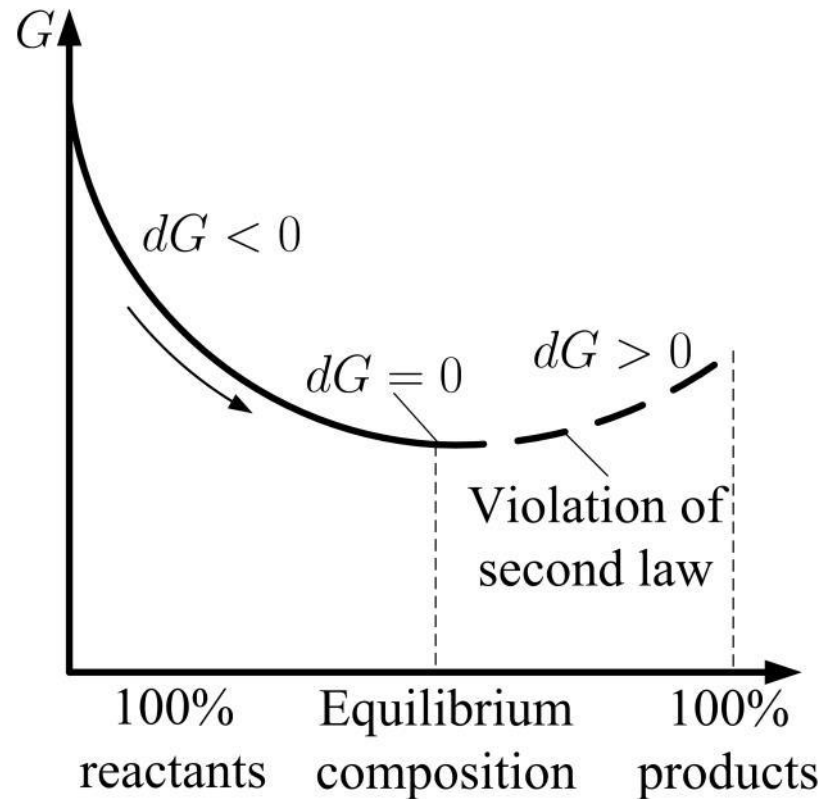
■ $(dG)_{T,P} = dH - TdS - SdT =$
$(dU + PdV + VdP) - TdS - SdT =$
$dU + PdV - TdS \leq 0$

Equilibrium criteria for a chemical reaction that takes place adiabatically.

Chemical and Phase Equilibrium （3）

Chemical and Phase Equilibrium （4）

- Speed of chemical reaction: $w = \dfrac{dc}{d\tau}$

- bB + dD ⇔ gG + rR
  - $w_1 = k_1 c_B^b c_D^d, w_2 = k_2 c_G^g c_R^r$
  - $w_1 = w_2, K_c = \dfrac{k_1}{k_2} = \dfrac{c_G^g c_R^r}{c_B^b c_D^d}, K_p = \dfrac{p_G^g p_R^r}{p_B^b p_D^d}$
  - $K_c = K_p (RT)^{-\Delta n}, \Delta n = g + r - b - d$
  - $K_p = \dfrac{n_G^g n_R^r}{n_B^b n_D^d} \left(\dfrac{p}{n}\right)^{g+r-b-d}$

Example 3