

# Week 6

Chemical reactions and  
combustion

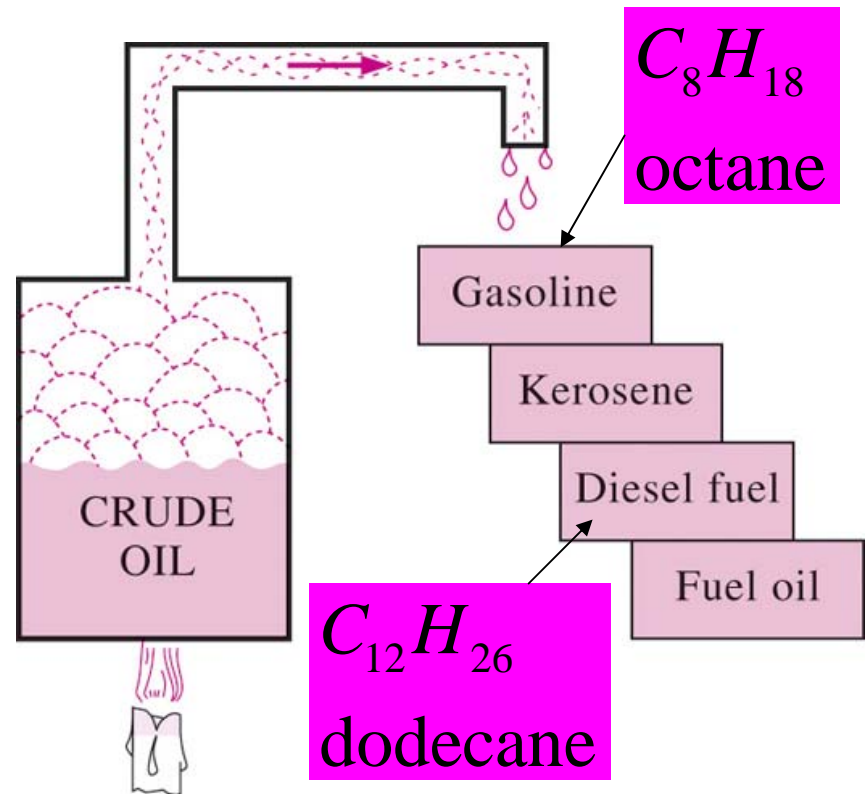
Thermodynamics of combustion

# Today's Outline

- Fuels and combustion
- Chemical reactions
- Mass conservation

# Fuels

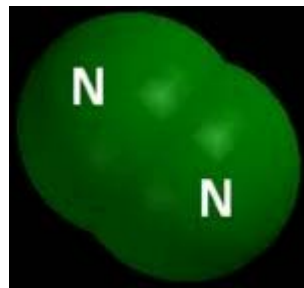
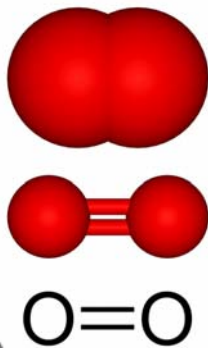
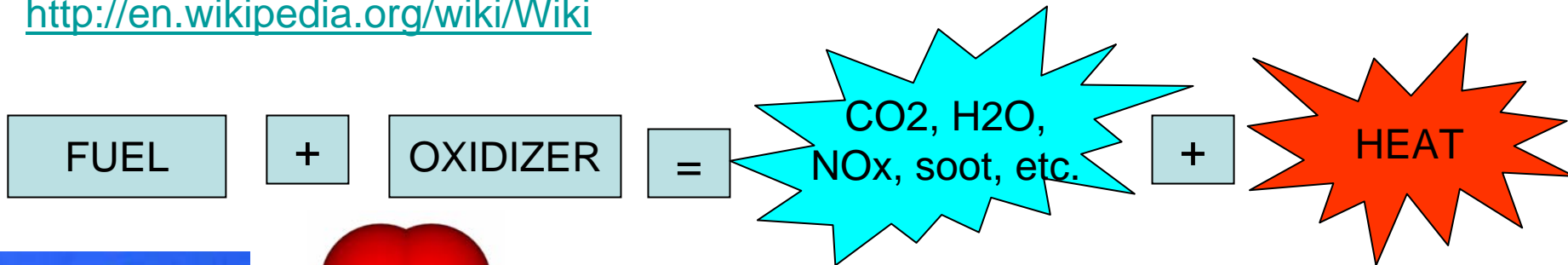
- Material capable of releasing energy when its chemical structure is changed or converted
- Most fuels made of hydrogen and carbon, e.g. hydrocarbons,  $C_nH_m$
- Coal(s), gasoline(l), natural gas(g)



# Combustion (“burning”)

*...is complex sequence of chemical reactions between fuel and oxidant accompanied by heat or both heat and light in form of glow or flame*

<http://en.wikipedia.org/wiki/Wiki>



# Flames



*Candle flame*



*Bunsen flames*



*Microgravity flames*

<http://en.wikipedia.org/wiki/Wiki>

# Laboratory turbulent flames



*Piloted jet flame* <http://www.ca.sandia.gov>

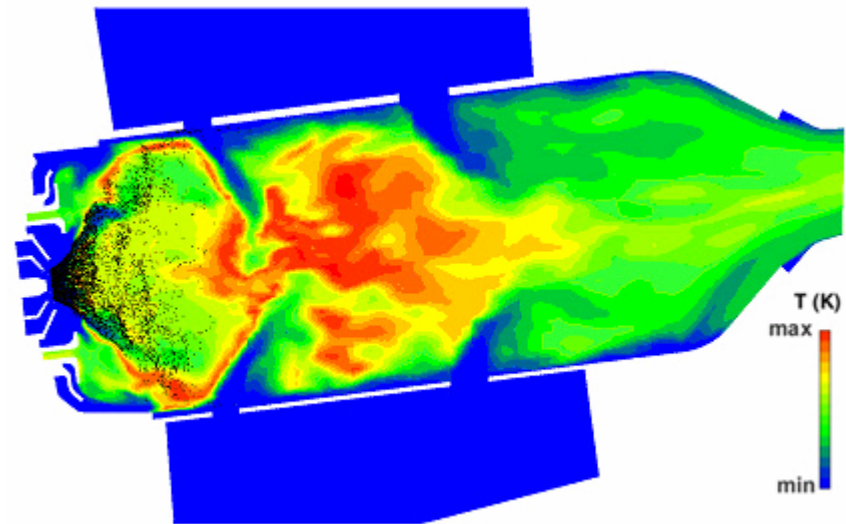


*Jet flame with recirculation*

# Air as an Oxidizer

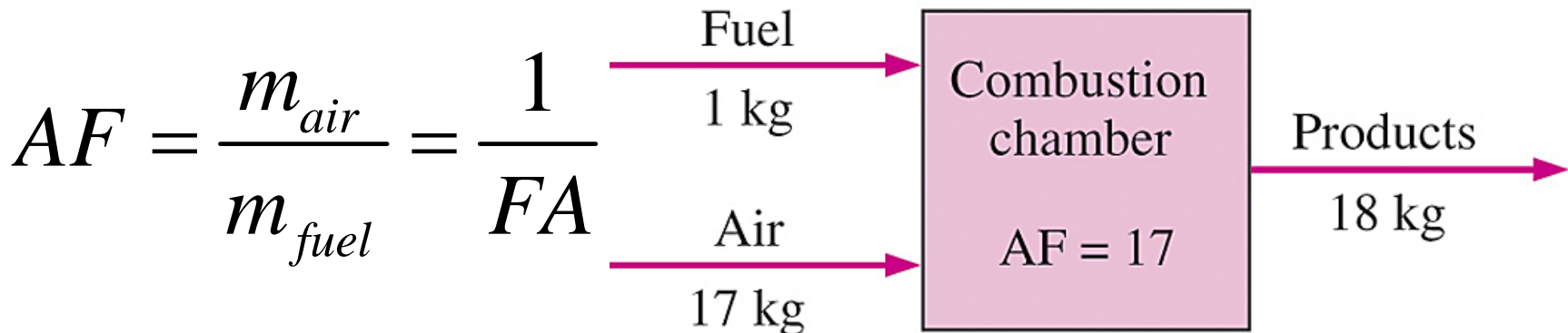
- Dry air modeled as 21% O<sub>2</sub>, 79% N<sub>2</sub> by mole numbers
- Each mole of oxygen entering combustion chamber comes with  $0.79/0.21 = 3.76$  moles of nitrogen

<http://www.cfdrc.com>



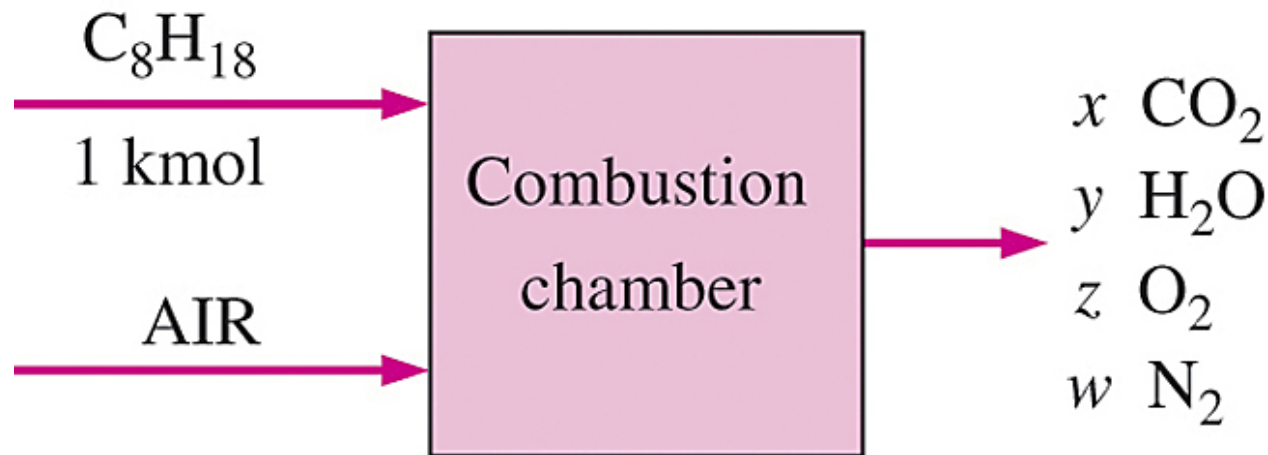
# Combustion Processes

- Nitrogen mostly inert (NO<sub>x</sub>) but has thermal effect
- Combustion air normally contains moisture
- Components before reaction, e.g. fuel, air, **reactants**
- Components after reaction, e.g. CO<sub>2</sub>, H<sub>2</sub>O, **products**
- Fuel must be above **ignition temperature** for burning e.g. 630 C for methane
- Total mass of each element conserved during a chemical reaction (total moles are not!  $m=NM$ )



# Example 15-1

- One kmole of octane is burned with air that contains 20 kmol of oxygen. Assuming the products contain only those species shown below, determine the mole number of each gas in the products and the air-fuel ratio for this combustion process.



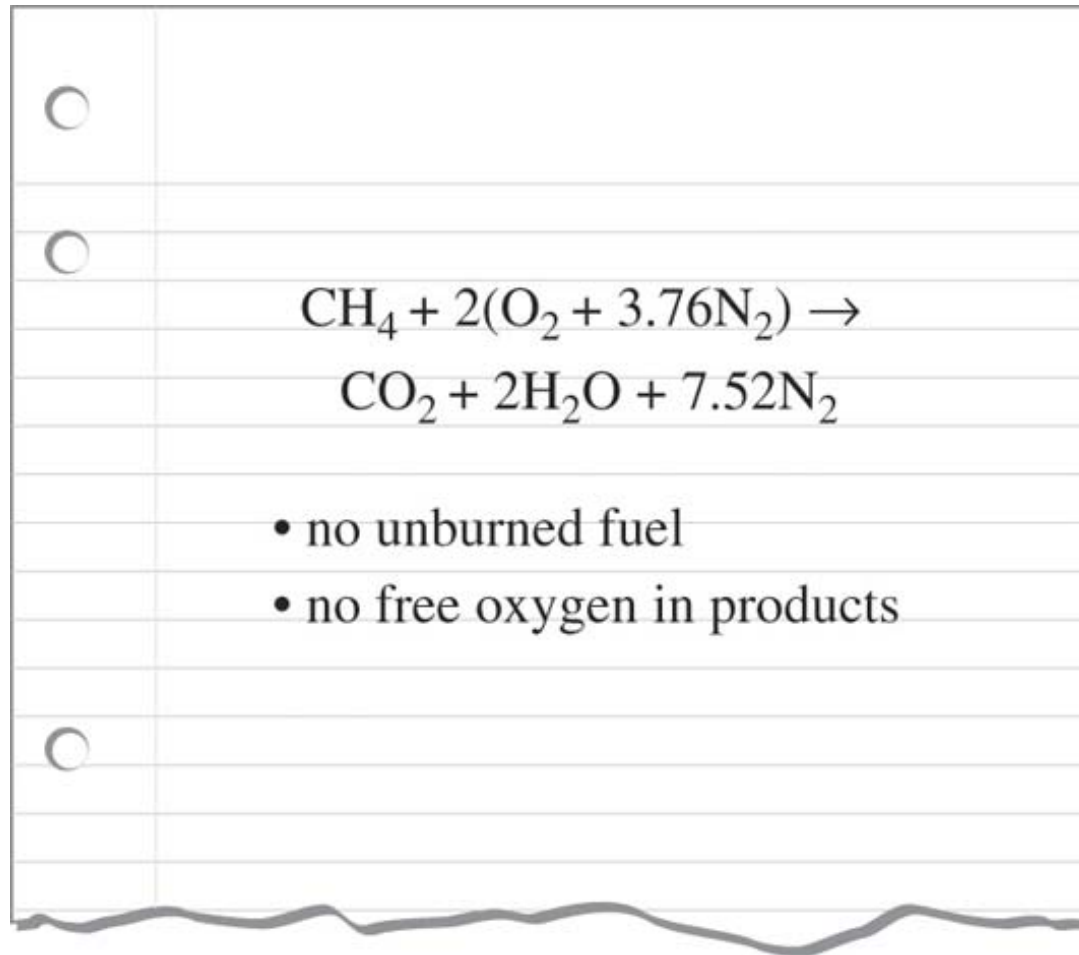
# Example 15-1

# Example 15-1

# Combustion Measures

- A combustion process is **complete** if all the carbon in the fuel burns to  $\text{CO}_2$  and all the hydrogen burns to  $\text{H}_2\text{O}^*$  (\*most likely)
- Incomplete if any unburned fuel or components such as C,  $\text{H}_2$ , CO, or OH left
- Causes? Insufficient oxygen or mixing, and dissociation
- Minimum amount of air needed for complete combustion is called **stoichiometric** or **theoretical air** e.g. chemically correct amount of air

# Stoichiometric Combustion Process



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

- no unburned fuel
- no free oxygen in products

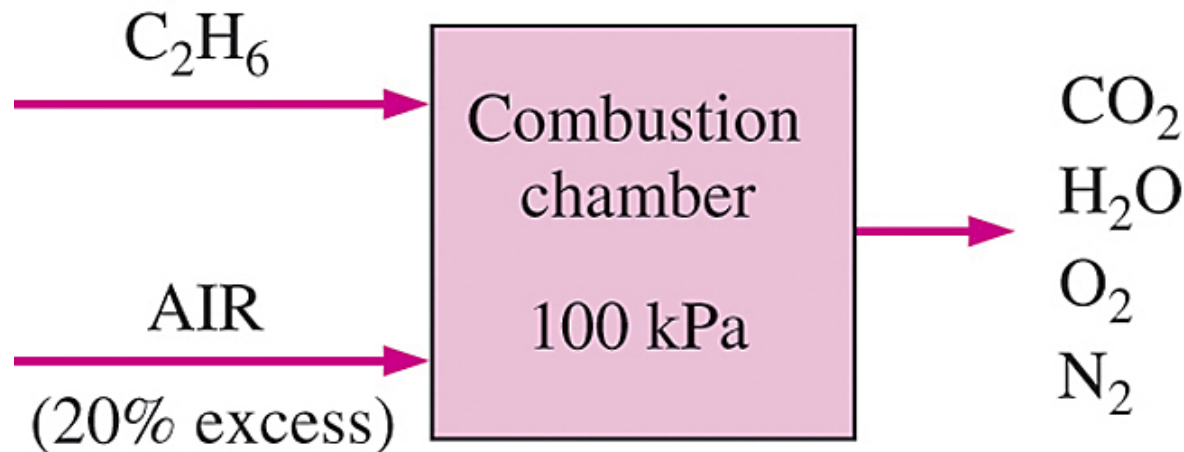
# More Combustion Measures

- The amount of air in excess of stoichiometric is called **excess air**
- Usually expressed as **percent excess air** or **percent theoretical air**
- For example,
  - 50% excess air = 150% theoretical air
  - 200% excess air = 300% theoretical air
- **Equivalence ratio** is ratio of actual FA ratio to stoichiometric FA ratio:

$$\varphi = \frac{(FA)_{actual}}{(FA)_{stoich.}}$$

# Example 15-2

- Ethane is burned with 20% excess air during a combustion process. Assuming complete combustion and a total pressure of 100 kPa, determine (a) the air-fuel ratio and (b) the dew-point temperature of the products.



# Example 15-2

# Example 15-2

# Summary

- Combustion involves chemical reaction(s) between reactants, fuel and oxidizer, producing products and a lot of heat
- $4.76 \text{ kmol air} = 1 \text{ kmol O}_2 + 3.76 \text{ kmol N}_2$
- Total mass (not moles) conserved during chemical reaction
- Complete combustion for hydrocarbon fuel implies products are  $\text{CO}_2$  and  $\text{H}_2\text{O}$
- Stoichiometric combustion is complete combustion with stoichiometric amount of air

# Today's Outline

- Enthalpy of formation/combustion
- First-law for reacting systems

# Chemical Reactions and Energy

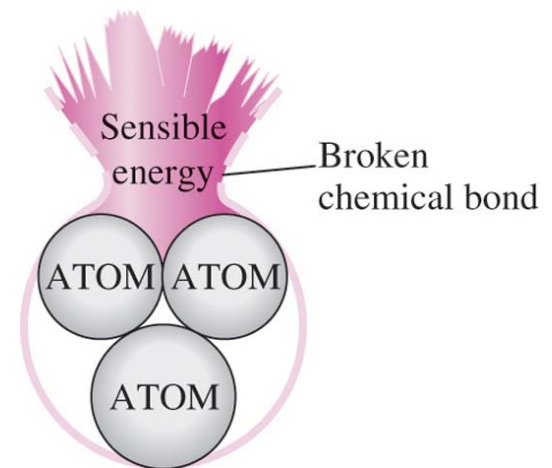
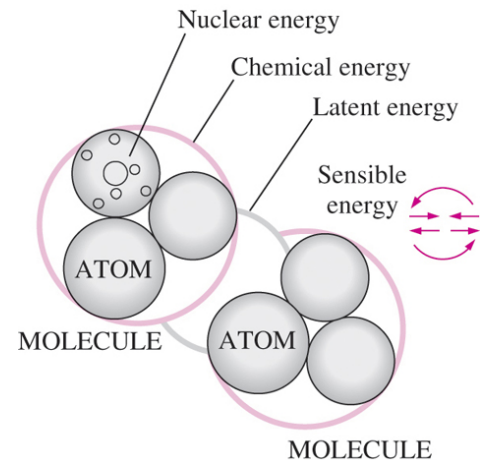
- During chemical reaction, molecular bonds broken, new ones form, resulting in chemical energy changes
- This must be accounted for in energy analysis

$$\Delta E_{sys} = \Delta E_{state} + \Delta E_{chem}$$

- Standard reference state (25 C (77 F) and 1 atm)  $h^\circ$

$$\bar{h}_{N_2, 500k} \rightarrow \bar{h}_{N_2, 500k} - \bar{h}_{N_2}^\circ$$

$$= 14,581 - 8669 = 5912 \text{ kJ} / \text{kmol}$$

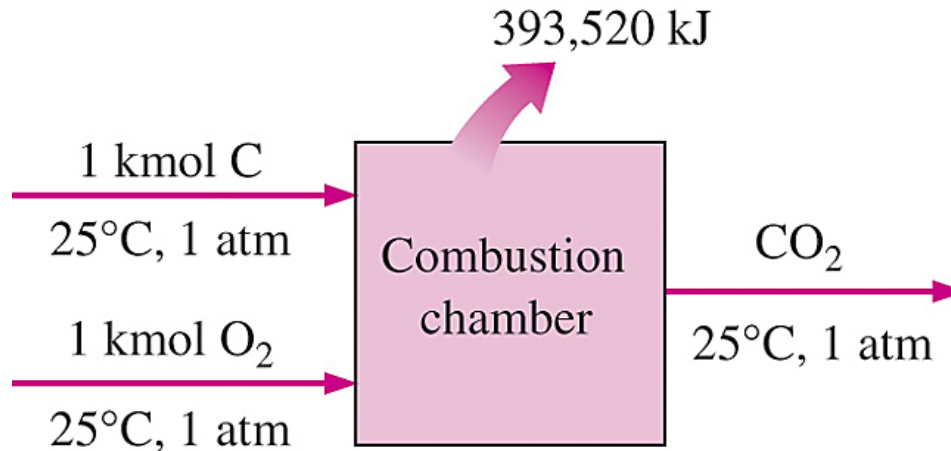


# Enthalpy of Reaction/Combustion

- Complete **exothermic** reaction:  $CO + 0.5O_2 \rightarrow CO_2$
- First law analysis:

$$Q = \Delta H = H_{prod} - H_{react} = -393,520 \text{ kJ / kmol}$$

- **Enthalpy of reaction**,  $h_R = -393,520 \text{ kJ/kmol}$
- **Enthalpy of combustion**,  $h_C = -393,520 \text{ kJ/kmol}$



*Enthalpy of combustion assumes complete combustion . . .*

# Enthalpy of Formation

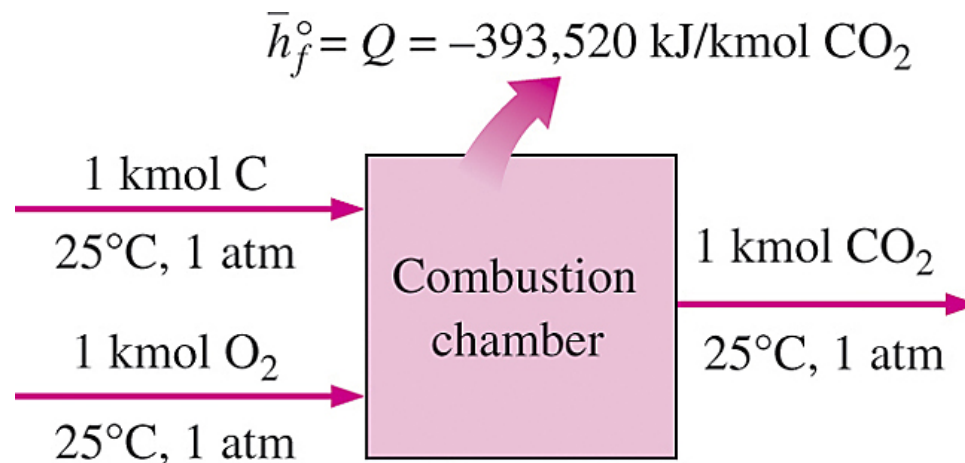
- Enthalpy of combustion of *limited value* due to wide range of fuels/fuel-mixtures and possibility of incomplete combustion
- Rather have measure of chemical energy of element or component . . .
- **Enthalpy of formation** is enthalpy of substance at a specified state due to its chemical composition
- We assign *enthalpy of formation of all stable elements*, e.g. O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and C, a value of zero at *standard reference state (SRS) (25 C, 1 atm)*

$$\bar{h}_f^o = 0 \text{ for stable elements at SRS}$$

# Enthalpy of Formation

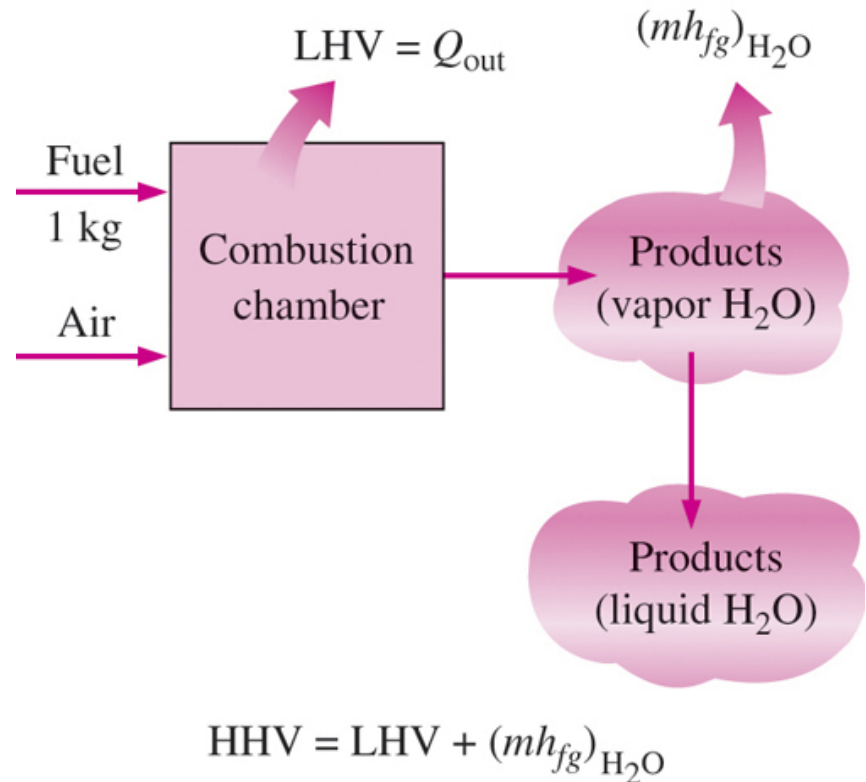
- Amount of energy absorbed/released as component is formed from its stable elements during steady-flow process at specified state

$$Q = H_{prod} - H_{react} = -393,520 \text{ kJ} / \text{kmol} = \bar{h}_{f,CO_2}^{\circ}$$



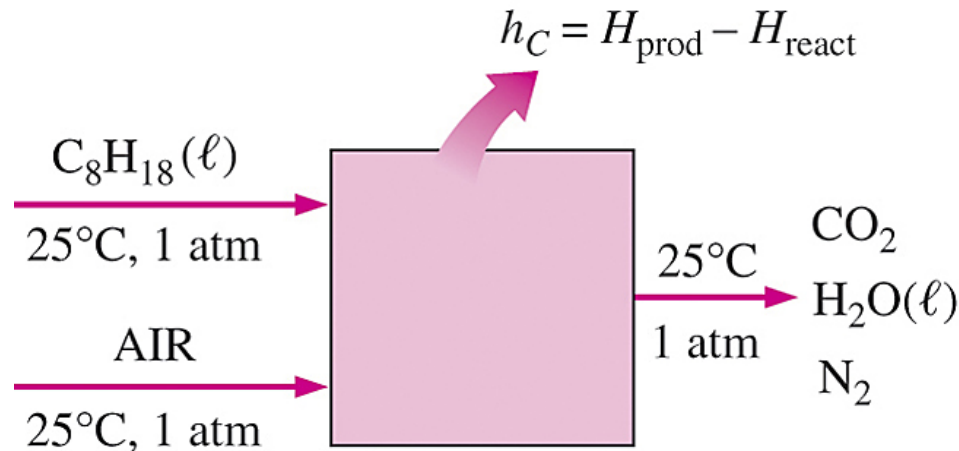
# Heating Value

- Amount of heat released when fuel burned completely in steady flow process and products returned to state of reactants
- Equal to absolute value of enthalpy of combustion e.g.  $HV = |h_c|$
- HHV (liquid  $H_2O$ ) vs. LHV (vapor  $H_2O$ )



# Example 15-5

- Determine the enthalpy of combustion of liquid octane at 25 C and 1 atm, using enthalpy of formation data from tables. Assume water in products is in liquid form.

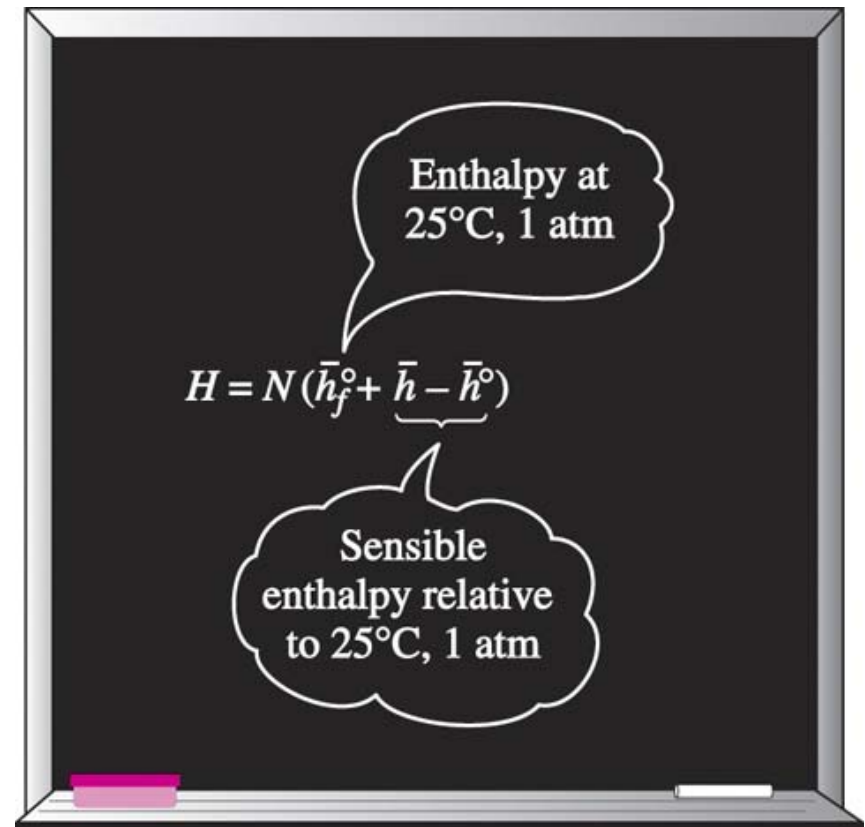


# Example 15-5

# Example 15-5

# First Law Analysis of Reacting Systems

- Need to express enthalpy so that it is:
  - relative to SRS
  - chemical energy appears explicitly
- Note: Enthalpy at SRS reduces to enthalpy of formation



# First Law Analysis of Reacting Systems

- Steady-flow energy balance:

$$0 = \dot{Q} - \dot{W} + \sum \dot{n}_r \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_r - \sum \dot{n}_p \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_p$$

- Per mole of fuel

$$0 = Q - W + \sum N_r \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_r - \sum N_p \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_p$$

- Rearrange:

$$Q - W = \sum N_p \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_p - \sum N_r \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_r$$

$$Q - W = H_{prod} - H_{react} \quad (\text{kJ} / \text{kmol fuel})$$

# Closed Systems

- Energy in – energy out = change in energy for system
- Avoid defining internal energy of formation

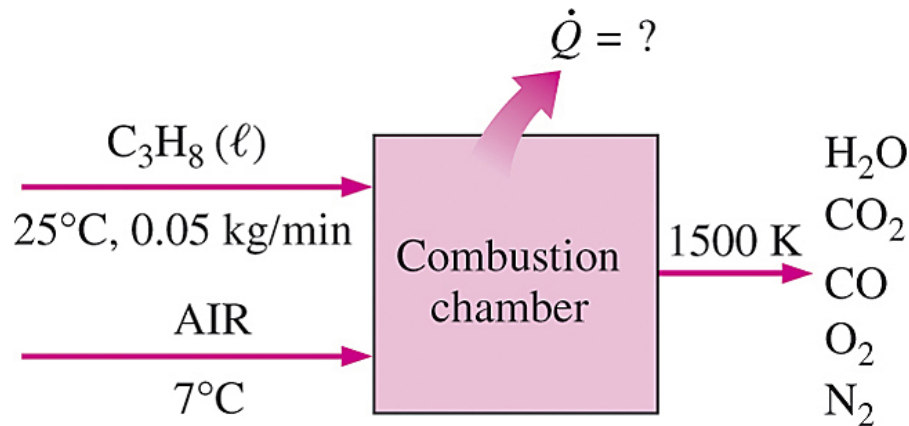
$$Q - W = U_{prod} - U_{react}$$

$$Q - W = \sum N_p \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v} \right)_p - \sum N_r \left( \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v} \right)_r$$

$$P\bar{v}_{\substack{\text{solids} \\ \text{liquids}}} \approx 0; \quad P\bar{v}_{\substack{\text{ideal} \\ \text{gas}}} = R_u T; \quad \bar{u} = \bar{h} - P\bar{v}$$

# Example 15-6

- Liquid propane enters a combustion chamber at 25 C at a rate of 0.05 kg/min where it is mixed and burned with 50% excess air that enters the combustion chamber at 7 C. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H<sub>2</sub>O but only 90% of the carbon burns to CO<sub>2</sub>, with the remaining 10% forming CO. If the exit temperature of the combustion gases is 1500K, determine (a) mass flow rate of air and (b) rate of heat transfer from combustion chamber.



# Example 15-6

# Example 15-6


# Example 15-6

# Summary

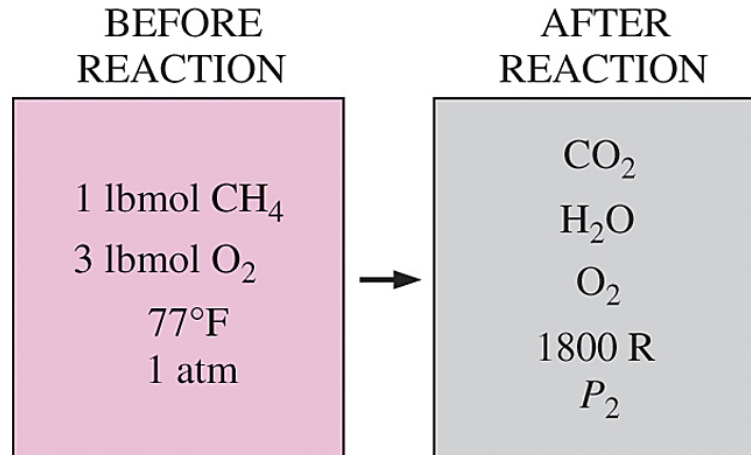
- For reacting systems, energy may change due to both (a) state (sensible) changes and (b) reaction (chemical)
- Need SRS due to composition changes
- To address changes in chemical energy we need to:
  - Explicitly include enthalpy of formation
  - Measure sensible energy relative to SRS

# Today's Outline

- Example - First law analysis for closed reacting system
- Adiabatic flame temperature

# Example 15-7

- The constant volume tank shown below contains 1 lbmol of methane gas and 3 lbmol of O<sub>2</sub> at 77 F and 1 atm. The contents of the tank are ignited, and methane gas burns completely. If the final temperature is 1800 R, determine (a) the final pressure in the tank and (b) the heat transfer during the process.



# Example 15-7

# Example 15-7

# Adiabatic Flame Temperature

- Without work interactions or changes in kinetic or potential energy, chemical energy released during a combustion process is:
  - Lost to the surroundings
  - Used internally to raise temperature of products of combustion
- The smaller the heat loss, the larger the temperature rise
- What about the limiting case? Zero heat loss,  $Q=0$ , so  $T_{\text{prod}}$  is called adiabatic flame temperature,  $T_p$  or  $T_f$

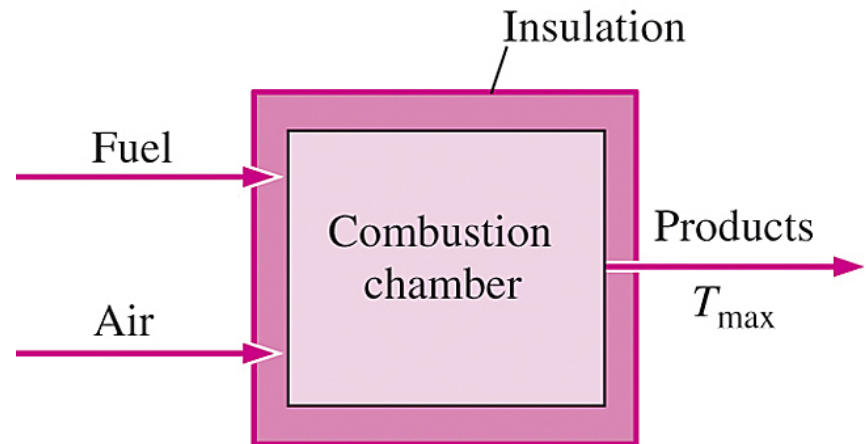
# Adiabatic Flame Temperature

- Maximum combustor temperature?
  - Complete combustion
  - Adiabatic conditions
- For steady flow, set  $Q=W=0$ :

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

$$\sum N_r \left( \bar{h}_f^o + \bar{h} - \bar{h}^o \right)_r = \sum N_p \left( \bar{h}_f^o + \bar{h} - \bar{h}^o \right)_p = \underbrace{f(T_P)}$$

- $T_P$ , adiabatic flame temperature



Non-linear function of reactant state, reaction completeness, amount of air

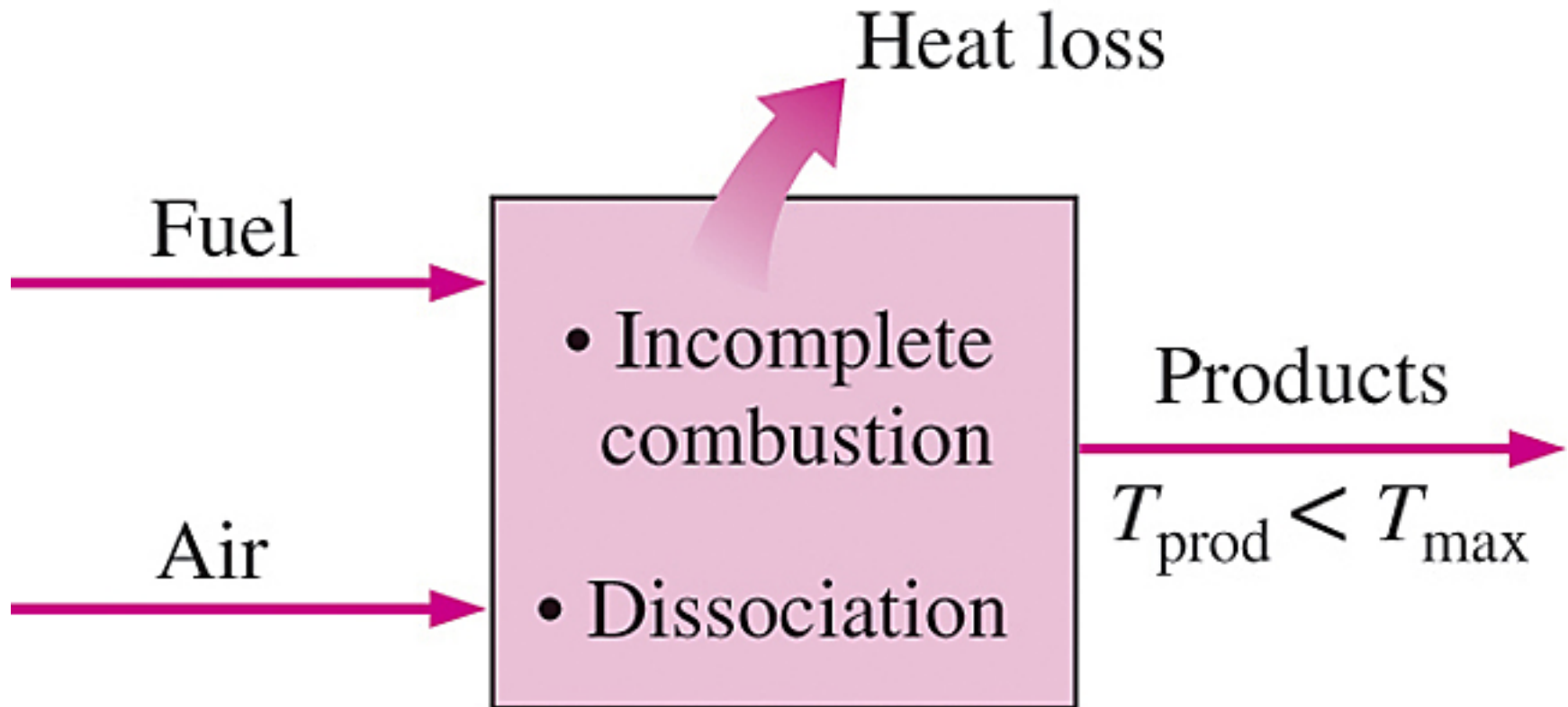
# Determine Adiabatic Flame Temperature - Procedure

- For given initial state of reactants,  $H_{\text{react}}$  can be found
- $H_{\text{prod}}$  depends on  $T_{\text{prod}}$  which is unknown
- Since dependence is implicitly nonlinear, an iterative approach is needed
  - Assume  $T_{\text{prod}}$
  - Find  $H_{\text{prod}}$
  - Is  $H_{\text{prod}} = H_{\text{react}}$
  - If yes,  $T_f = T_{\text{prod}}$  – stop, else go to 1 and repeat

# Notes

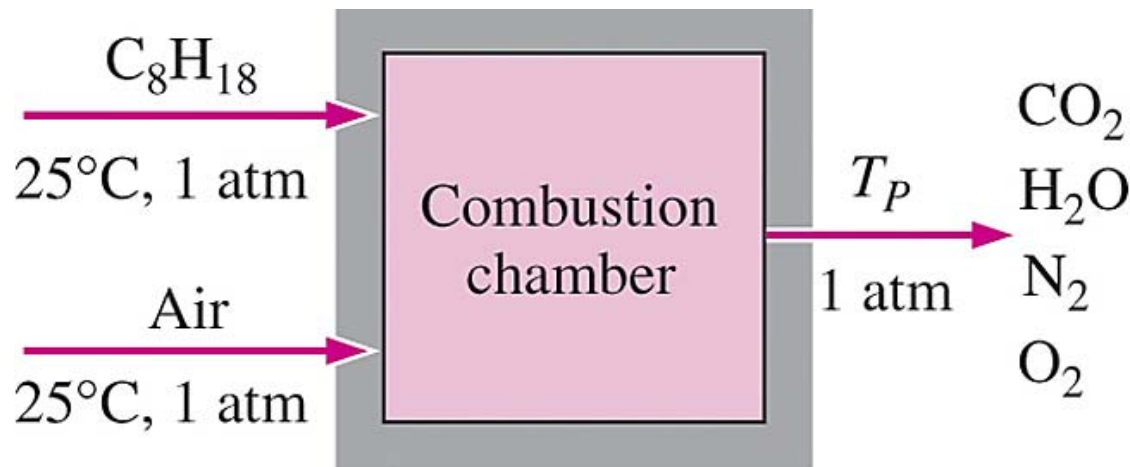
- With air as oxidant product gases are mostly  $N_2$ , so a good guess for  $T_{\text{prod}}$  is obtained by assuming all product species are  $N_2$
- $T_f$  important because maximum temperature is fixed by metallurgical limits
- $T_{\text{max}} < T_f$  due to incomplete combustion, heat loss, dissociation at high  $T$
- $T_f = f(\text{state of reactants, degree of completion of reaction (energy release), amount of air used})$
- $T_f$  attains maximum when complete combustion with theoretical air occurs
- Finding  $T_f$  is easy with EES . . . .

# Factors that Lower Combustor Temperatures



# Example 15-8

- Liquid octane enters combustion chamber of a gas turbine steadily at 1 atm, 25 C, and it is burned with air that enters the combustion chamber at the same state. Determine the adiabatic flame temperature for (a) complete combustion with 100% theoretical air, (b) complete combustion with 40% theoretical air, and (c) incomplete combustion (some CO in the products) with 90% theoretical air



# Example 15-8

# Example 15-8


# Example 15-8

# Example 15-8

# Example 15-8

# Example 15-8

# Summary

- In absence of heat loss to surroundings, product temperature will reach a maximum called adiabatic flame temperature
- Determined from steady-flow energy analysis via iteration
- Maximized for stoichiometric combustion