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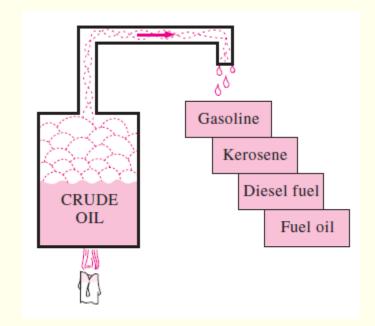
- •The combustion process is a chemical reaction whereby fuel is oxidized and energy is released.
- •Fuels are composed of some compound or mixture containing carbon, and H<sub>2</sub>.
- e.g. CH<sub>4</sub> Methane, C<sub>8</sub>H<sub>18</sub>-Octane, Coal, Mixture of C, H<sub>2</sub>, S, O<sub>2</sub>, N<sub>2</sub> and non-combustibles





#### **Fuels**

- Hydrocarbons  $-C_nH_m$  Most familiar fuels consist primarily of hydrogen and carbon. They exist in all phases, some examples being coal, gasoline, NG.
- Gasoline is treated as octane, C<sub>8</sub>H<sub>18</sub>, and the diesel fuel as dodecane,
   C<sub>12</sub>H<sub>26</sub>. Methane (NG)
- (LPG) is a byproduct of natural gas processing or the crude oil refining. It consists mainly of propane





#### **Fuels and Combustion**

- Any material that can be burnt Fuel. Coal is a major fuel. Coal composition varies from place to place.
- Most liquid fuels are obtained from fractional distillation of Crude oil (Petroleum) from where we get Gasoline (Petrol -Octane,  $C_8H_{18}$ ), Diesel (Dodecane  $C_{12}H_{26}$ ), methanol (CH<sub>3</sub>OH) etc.
- Natural Gas Mainly Methane and other HC. > CNG or LNG. It may be stored as pressurised gas (150-200 atm)as CNG on in liquid phase as LNG (-162°C)
- LPG byproduct of crude oil refining. Mainly Propane plus other HC.
- Ethanol, Methonal are used as additives in gasoline to reduce air pollution

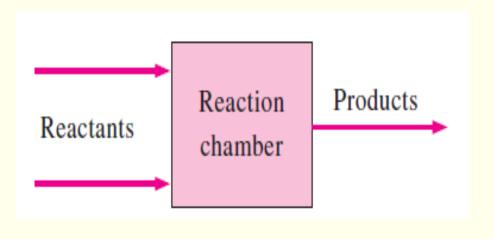


## **Comparison of Fuels**

Fuel	Energy Content kJ/L	Gasoline Equivalence* L/L -Gasoline
Gasonline	31,850	1
Light diesel	33,170	0.96
Heavy diesel	35,800	0.89
LPG (Liquefied petroleum gas Primarily propane	23,410	1.36
Ethanol (or ethyl alcohol)	29,420	1.08
Methanol (or methyl alcohol)	18,210	1.75
CNG (Compressed natural gas, primarily methane, at 200 atm)	8,080	3.94
LNG (Liquid natural gas, Primarily methane)	20,490	1.55

<sup>\*</sup> Amount of fuel whose energy content is equal to the energy content of 1-L gasoline





- Consider only those reactions that go to completion.
- The components prior to the reaction are called reactants
- The components after the reaction are called products.
- Reactants  $\rightarrow$  Products

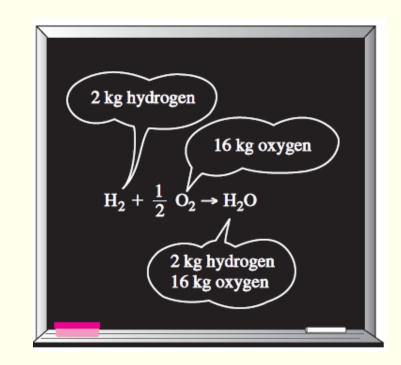


 In a complete or stoichiometric combustion, all carbon is burned to carbon dioxide (CO<sub>2</sub>) & Hydrogen is converted into water (H<sub>2</sub>O).

• e.g.

$$C + O_2 \rightarrow CO_2$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$





- A combustion process is complete if all the carbon in the fuel burns to  $CO_2$ , all the hydrogen burns to  $H_2O$ .
- The combustion process is **incomplete** if the combustion products contain any unburned fuel or components such as C, H2, CO, or OH.
- A complete combustion of octane in oxygen is represented by balanced combustion equation. The balanced combustion equation is obtained by making sure same number of atoms of each element on both sides of the equation. ⇒ the mass is conserved.



- $\begin{array}{ccc} \bullet & C_8H_{18} + A\,O_2 \rightarrow B\,CO_2 + \\ & D\,H_2O \end{array}$
- Often balance the C and H for complete combustion by inspection

$$C_8H_{18} + AO_2 \rightarrow 8CO_2 + 9H_2O$$

• The amount of oxygen is found from the oxygen balance.

• It is better to conserve species on a monatomic basis

*O*: 
$$A(2) = 8(2) + 9(1)$$
  
 $A = 12.5$ 

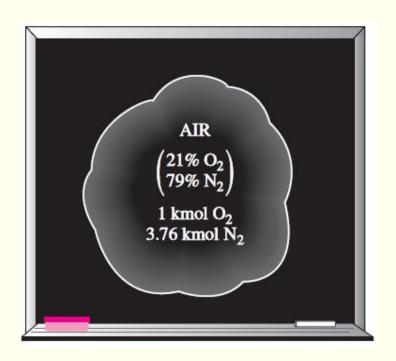
$$C_8H_{18} + 12.5 O_2$$
  
 $\rightarrow 8 CO_2 + 9 H_2O$ 

 Mole numbers are not conserved, but the mass is conserved on a total basis as well as a specie basis.



- Complete combustion process is also called stoichiometric combustion, & all coefficients are called the stoichiometric coefficients
- The minimum amount of air needed for the complete combustion is called the **stoichiometric** or **theoretical air.**
- In most combustion processes, oxygen is supplied in the form of air rather than pure oxygen.
- Air = 21 %  $O_2$  & 79 %  $N_2$  on a volume basis.





For ideal gas mixtures,

$$\frac{\%}{V} = \frac{\%}{mole}$$

• Thus, for each mole of oxygen in air, 79/21 = 3.76 kmoles of nitrogen.

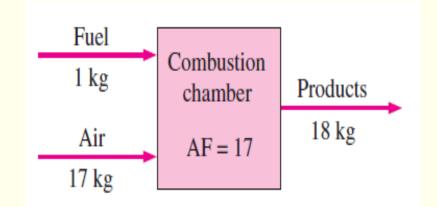
• Complete or theoretical combustion of octane with air – apply for  $C_8H_{18}$ 

$$C_8H_{18} + 12.5 (O_2 + 3.76 N_2) \rightarrow$$
  
 $8 CO_2 + 9 H_2O + 47 N_2$ 



#### Air-Fuel Ratio

- total moles of a mixture = sum of moles of each component.
- 12.5(1 + 3.76) = 59.5 moles of air required for each mole of fuel for the complete combustion process.





#### **AF Ratio**

- Often complete combustion of the fuel will not occur unless there is an excess of air present greater than just the theoretical air required for complete combustion.
- To determine the amount of excess air supplied for a combustion process, the air-fuel ratio AF defined as

$$AF = \frac{kmol\,air}{kmol\,fuel}$$



## **Air Fuel Ratio**

• Thus, for the above example, theoretical air-fuel ratio is

$$AF_{th} = \frac{12.5(1+3.76)}{1} = 59.5 \frac{kmol \, air}{kmol \, fuel}$$



## Air to Fuel Ratio

• On a mass basis, the theoretical air-fuel ratio is

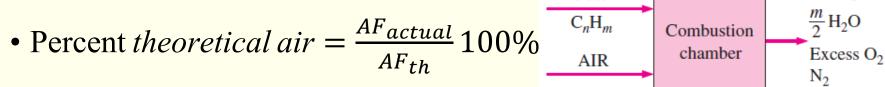
$$AF_{th} = 59.5 \frac{kmol \, air}{kmol \, fuel} \frac{28.97 \, \frac{kg \, air}{kmol \, air}}{[8(12) + 18(1)] \frac{kg \, fuel}{kmol \, fuel}}$$

$$= 15.12 \frac{kg \, air}{kg \, fuel}$$



## % Theoretical and Excess Air for Combustion

- •Generally more than theoretical air is supplied to ensure complete combustion and to reduce or eliminate CO in the exhaust.
- The amount of excess air is expressed as percent theoretical air and percent excess air.



Fuel

n CO<sub>2</sub>

• Percent excess 
$$air = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$



• Show that these results may be expressed in terms of the moles of oxygen only as

Percent theoretical air = 
$$\frac{N_{O_2 \ actual}}{N_{O_2 \ th}} 100\%$$

Percent excess air = 
$$\frac{N_{O_2 \ actual} - N_{O_2 \ th}}{N_{O_2 \ th}} 100\%$$



## **Excess Air Combustion**

• The combustion equation for complete combustion of octane with 120 percent theoretical air (20 percent excess air).

• Note that 1.2 Stochiometric O<sub>2</sub> is required for complete combustion to produce 8 kmol of carbon dioxide and 9 kmol of water; therefore, (0.2)(Stoi)O<sub>2</sub> is found as excess oxygen in the products.



#### **Excess Air Combustion**

Balance the equation for excess Air

$$C_8H_{18} + 1.2A_{th} (O_2 + 3.76 N_2) \rightarrow$$
  
8  $CO_2 + 9 H_2O + 0.2A_{th} O_2 + 1.2A_{th} (3.76) N_2$ 

• 
$$0$$
:  $1.2A_{th}(2) = 8(2) + 9(1) + 0.2A_{th}(2)$ 

$$A_{th} = 12.5$$



## **Incomplete Combustion - problem**

• Combustion of  $C_8H_{18}$  with 120 % theoretical air where 80 % C in the fuel goes into  $CO_2$ . (Write the equation and balance)

$$C_8H_{18} + 1.2(12.5) (O_2 + 3.76 N_2) \rightarrow$$
  
 $0.8(8) CO_2 + 0.2(8) CO + 9 H_2O + X O_2 + 1.2(47) N_2$ 

• O balance gives

$$0: \quad 1.2(12.5)(2) = 0.8(8)(2) + 0.2(8)(1) + 9(1) + X(2)$$

$$X = 3.3$$

$$C_8H_{18} + 1.2(12.5) (O_2 + 3.76 N_2) \rightarrow$$

$$6.4 CO_2 + 1.6 CO + 9 H_2O + 3.3 O_2 + 1.2(47) N_2$$



## Product Gas Analysis is known

- Combustion Equation When Product Gas Analysis Is Known
- Propane gas C<sub>3</sub>H<sub>8</sub> is reacted with air such that the dry product gases are 11.5 percent CO<sub>2</sub>, 2.7 percent O<sub>2</sub>, and 0.7 percent CO by volume.
- What percent theoretical air was supplied?
- What is the dew point temperature of the products if the product pressure is 100 kPa?



• Assume 100 kmol of dry product gases; then the percent by volume can be interpreted to be mole numbers. But how much fuel and air were supplied or water formed to get the 100 kmol of dry product gases are not known.

$$X C_3 H_8 + A (O_2 + 3.76 N_2) \rightarrow$$
  
11.5  $CO_2 + 0.7 CO + 2.7 O_2 + B H_2 O + A(3.76) N_2$ 

• The unknown coefficients A, B, and X are found by conservation of mass for each species.



$$X C_3 H_8 + A (O_2 + 3.76 N_2) \rightarrow$$
  
11.5  $CO_2 + 0.7 CO + 2.7 O_2 + B H_2 O + A(3.76) N_2$ 

C: 
$$X(3) = 11.5(1) + 0.7(1)$$
  $X = 4.07$ 

$$H: X(8) = B(2)$$
  $B = 16.28$ 

*O*: 
$$A(2) = 11.5(2) + 0.7(1) + 2.7(2) + B(1)$$
  $A = 22.69$ 

$$N_2$$
:  $A(3.76) = 85.31$ 

• The balanced equation is

$$4.07 C_3 H_8 + 22.69 (O_2 + 3.76 N_2) \rightarrow$$
  
 $11.5 CO_2 + 0.7 CO + 2.7 O_2 + 16.28 H_2 O + 85.31 N_2$ 



- Second method to find the coefficient A:
- Assume the remainder of the 100 kmol of dry product gases is  $N_2$ .

$$kmol\ N_2 = 100 - (11.5 + 0.7 + 2.7) = 85.1$$

• Then A is:  $A = \frac{85.1}{3.76} = 22.65$  (fairly good check)



- •These two methods don't give the same results for A, but they are close.
- •What would be the units on the coefficients in the balanced combustion equation?
- •To simplify this calculation it is generally better to write the combustion equation per kmol of fuel. To write the combustion equation per unit kmol of fuel, divide by 4.07:



$$C_3H_8 + 5.57 (O_2 + 3.76 N_2) \rightarrow$$
  
2.83  $CO_2 + 0.17 CO + 0.66 O_2 + 4.0 H_2O + 20.96 N_2$ 

The actual air-fuel ratio is

$$AF_{actual} = \frac{(5.57)(1+3.76)kmol\,air\,\,28.97\,\frac{kg\,air}{kmol\,air}}{1kmol\,fuel[3(12)+8(1)]\frac{kg\,fuel}{kmol\,fuel}}$$

$$= 17.45 \frac{kg \, air}{kg \, fuel}$$



•The theoretical combustion equation is

$$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow$$
  
  $3CO_2 + 4.0H_2O + 18.80N_2$ 

•The theoretical air-fuel ratio is

$$AF_{th} = \frac{(5)(1+3.76)kmol \, air \, 28.97 \, \frac{kg \, air}{kmol \, air}}{1kmol \, fuel[3(12)+8(1)] \frac{kg \, fuel}{kmol \, fuel}}$$
$$= 15.66 \frac{kg \, air}{kg \, fuel}$$



•The percent theoretical air is

Percent theoretical air = 
$$\frac{AF_{actual}}{AF_{th}} 100\%$$
$$= \frac{17.45}{15.66} 100 = 111\%$$

Or

Percent theoretical air = 
$$\frac{N_{O_{2actual}}}{N_{O_{2th}}} 100\%$$
$$= \frac{5.57}{5} 100 = 111\%$$



• The percent excess air is

Percent excess air = 
$$\frac{AF_{actual} - AF_{th}}{AF_{th}}$$
 100%  
=  $\frac{17.45 - 15.66}{15.66}$  100 = 11%

- •Dew Point Temperature
- •The dew point temperature for the product gases is the temperature at which the water in the product gases would begin to condense when the products are cooled at constant pressure. The dew point temperature is equal to the saturation temperature of the water at its partial pressure in the products.

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#### **DPT**

$$T_{dp} = T_{sat} at P_{v} = y_{v} P_{products}$$
$$y_{v} = \frac{N_{water}}{\sum_{products} N_{e}}$$

•Determine dew point temperature of the products

$$y_v = \frac{4}{2.83 + 0.17 + 0.66 + 4 + 20.96} = 0.1398$$

$$P_v = y_v P_{products} = 0.1398(100 \, kPa) = 13.98 \, kPa$$

$$T_{dp} = T_{Sat}$$
 at  $13.98 \, \text{kPa} = 52.31^{\circ} \, \text{C}$ 



## **Combustion Gas Analyser**

- Orsat gas analyzer Commonly used device
- Process: The ratio of the reduction in volume to the original volume is the volume fraction of the gas equivalent to the mole fraction.
- In Orsat analysis, the gas sample is collected over water and is maintained saturated at all times. Therefore, the vapor pressure of water remains constant during the entire test.
- For this reason the presence of water vapor in the test chamber is ignored and data are reported on a dry basis.
- However, the amount of H<sub>2</sub>O formed during combustion is easily determined by balancing the combustion equation.



# **Reverse Combustion Analysis**

- •An unknown hydrocarbon fuel,  $C_XH_Y$  is reacted with air such that the dry product gases are 12.1 percent  $CO_2$ , 3.8 percent  $O_2$ , and 0.9 percent CO by volume. What is the average makeup of the fuel?
- Assume 100 kmol of dry product gases; then the percent by volume can be interpreted to be mole numbers.

$$C_X H_Y + A (O_2 + 3.76 N_2) \rightarrow$$

$$12.1 CO_2 + 0.9 CO + 3.8 O_2 + B H_2 O + D N_2$$



$$C_X H_Y + A (O_2 + 3.76 N_2) \rightarrow$$
  
12.1  $CO_2 + 0.9 CO + 3.8 O_2 + B H_2 O + D N_2$ 

• The five unknown coefficients *A*, *B*, *D*, *X*, and *Y* are found by conservation of mass for each species, *C*, *H*, *O*, and *N* plus one other equation. Here use the subtraction method for the nitrogen to generate the fifth independent equation for the unknowns.



$$C_X H_Y + A (O_2 + 3.76 N_2) \rightarrow$$
  
12.1  $CO_2 + 0.9 CO + 3.8 O_2 + B H_2O + D N_2$ 

•The unknown coefficients *A*, *B*, *D*, *X*, and *Y* are found by conservation of mass for each species. Here assume the remainder of the dry product gases is nitrogen.

$$N_2$$
:  $D = 100 - (12.1 + 0.9 + 3.8) = 83.2$ 



$$C_X H_Y + A (O_2 + 3.76 N_2) \rightarrow$$
  
12.1  $CO_2 + 0.9 CO + 3.8 O_2 + B H_2O + D N_2$ 

$$O_2$$
:  $A = \frac{D}{3.76} = \frac{83.2}{3.76} = 22.13$ 

*O*: 
$$A(2) = (12.1)(2) + (0.9)(1) + (3.8)(2) + B(1)$$
  
 $B = 11.54$ 

$$C: 1(X) = 12.1(1) + (0.9)(1)$$

$$X = 13.0$$

$$H: 1(Y) = B(2) \rightarrow Y = 23.08$$



The balanced equation is

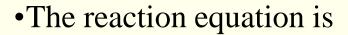
$$C_{13}H_{23.08} + 22.13 (O_2 + 3.76 N_2) \rightarrow$$
  
 $12.1 CO_2 + 0.9 CO + 3.8 O_2 + 11.54 H_2O + 83.2 N_2$ 



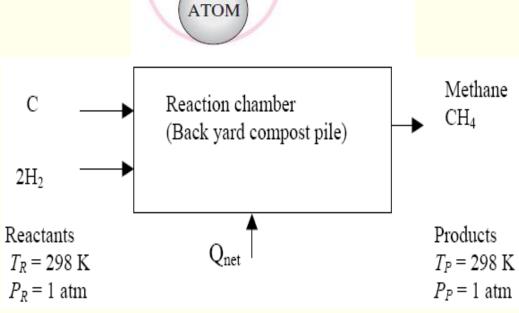
- •When a compound is formed from its elements heat transfer occurs.
- •When heat is given off, the reaction is called **exothermic**.
- The process involves no work interactions.
- From the steady-flow energy balance relation, the heat transfer during combustion must be equal to the difference between the enthalpy of the products and the enthalpy of the reactants Enthalpy of combustion



When heat is required, the reaction is called endothermic. Consider the following.



$$C + 2H_2 \rightarrow CH_4$$



Sensible

energy

ATOM ATOM

Broken

chemical bond



• The conservation of energy for a steady-flow combustion process is :

$$E_{in} = E_{out}$$

$$Q_{net} + H_{Reactants} = H_{Products}$$

$$Q_{net} = H_{Products} - H_{Reactants}$$

Enthalpy of reaction:  $H_R$  is defined as 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.



$$Q_{net} = \sum_{Products} N_e \, \bar{h}_e - \sum_{Reactants} N_i \, \bar{h}_i$$

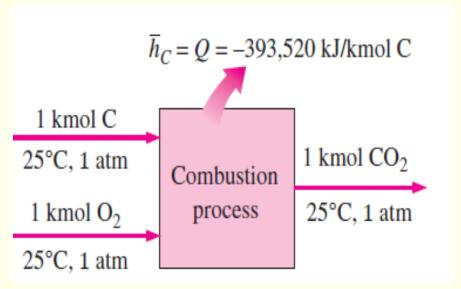
$$Q_{net} = 1\overline{h}_{CH_4} - \left(1\overline{h}_C + 2\overline{h}_{H_2}\right)$$

•A common reference state for the enthalpies of all reacting components is established.



### **Enthalpy of Combustion and Formation**

- It 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 T, P.
- Enthalpy of Combustion is different for different fuels and mixtures. So no practical values are available.
- More fundamental property, h<sub>f</sub>



Enthalpy of formation, h<sub>f</sub>, is the enthalpy of a substance at a specified state due to its chemical composition



•The enthalpy of the elements or their stable compounds is defined to be ZERO at 25 °C (298 K) and 1 atm (or 0.1 MPa).

$$Q_{net} = 1\bar{h}_{CH_4} - (1(0) + 2(0)) = \bar{h}_{CH_4}$$

- •This heat transfer is called the **enthalpy of formation** for methane,  $\bar{h}_f^o$ . The superscript (o) implies the 1 atm pressure value and the subscript (f) implies 25 °C data,  $\bar{h}_f^o$  is given in the Table.
- •During the formation of methane from the elements at 298 K, 0.1 MPa, heat is given off (an exothermic reaction).



$$Q_{net} = \bar{h}_{fCH_4}^o = -74,850 \frac{kJ}{kmol_{CH_4}}$$

- •The enthalpy of formation  $\bar{h}_f^o$  is tabulated for typical compounds.
- •The enthalpy of formation of the elements in their stable form is taken as zero.
- •The enthalpy of formation of the elements found naturally as diatomic elements, such as nitrogen, oxygen, and hydrogen, is defined to be zero.



# The enthalpies of formation for several combustion components are given in the following table.

Substance	Formula	M	kJ/kmol
Air		28.97	0
Oxygen	$O_2$	32	0
Nitrogen	$N_2$	28	0
Carbon dioxide	$CO_2$	44	-393,520
Carbon monoxide	СО	28	-110,530
Water (vapor)	$H_2O_{vap}$	18	-241,820
Water (liquid)	$H_2O_{liq}$	18	-285,830
Methane	CH <sub>4</sub>	16	-74,850
Acetylene	$C_2H_2$	26	+226,730
Ethane	$C_2H_6$	30	-84,680
Propane	$C_3H_8$	44	-103,850
Butane	$C_4H_{10}$	58	-126,150
Octane (vapor)	$C_8H_{18}$	114	-208,450
Dodecane	$C_{12}H_{26}$	170	-291,010



- The enthalpies are calculated relative to a common base or reference called the enthalpy of formation.
- The enthalpy of formation is the heat transfer required to form the compound from its elements at 25 °C at 1 atm.
- The enthalpy at any other temperature is given as

$$\bar{h} = \bar{h}_f^o + (\bar{h}_T - \bar{h}^o)$$

• Here the term  $\bar{h}^o$  is the enthalpy of any component at 298 K.



- The enthalpies at the temperatures *T* and 298 K are given in Table.
- If tables are not available, the enthalpy difference due to the temperature difference can be calculated from

$$(\bar{h}_T - \bar{h}^\circ) = \int_{298K}^T \bar{C}_p \, dT' = \bar{C}_{p,ave}(T - 298)$$



# I Law application - Combustion

• Based on the classical sign convention, the net heat transfer to the reacting system is

$$Q - W = H_{\text{prod}} - H_{\text{react}} \qquad \text{(kJ/kmol fuel)}$$
 
$$H_{\text{prod}} = \sum N_p (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ})_p \qquad \text{(kJ/kmol fuel)}$$
 
$$H_{\text{react}} = \sum N_r (\overline{h}_f^{\circ} + \overline{h} - \overline{h}^{\circ})_r \qquad \text{(kJ/kmol fuel)}$$
 
$$Q_{net} = H_P - H_R$$

$$=\sum_{Products}N_{e}[\bar{h}_{f}^{o}+(\bar{h}_{T}-\bar{h}^{o})]_{e}-\sum_{Reactants}N_{i}[\bar{h}_{f}^{o}+(\bar{h}_{T}-\bar{h}^{o})]_{i}$$

• In an actual combustion process, is the value of  $Q_{net}$  positive or negative?



•Butane gas C<sub>4</sub>H<sub>10</sub> is burned in theoretical air as shown below. Find the net heat per kmol of fuel.

Fuel Combustion Chamber

CO2 H2O N2

Theoretical air

Reactants  $T_R = 298 \text{ K}$   $P_R = 1 \text{ atm}$ CO2 H2O N2

Products  $T_P = 1000 \text{ K}$   $P_P = 1 \text{ atm}$ 

•Balanced combustion equation:

$$C_4H_{10} + 6.5(O_2 + 3.76N_2) \rightarrow$$

$$4CO_2 + 5H_2O + 24.44N_2$$



$$Q_{\text{net}} = \sum_{Products} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{Reactants} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e$$



•Reactants: TR = 298 K

Comp	$N_i$ kmol/kmol fuel	kJ/kmol $ar{h}_f^o$	kJ/kmol $ar{h}_T$	kJ/kmol $ar{h}^o$	kJ/kmol fuel $N_i \left[ \bar{h}_f^o + (\bar{h}_T - \overline{h}^o) \right]_i$
$C_4H_{10}$	1	-126,150			-126,150
$O_2$	6.5	0	8,682	8,682	0
$N_2$	24.44	0	8,669	8,669	0

$$H_R = \sum_{\substack{Reactants}} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$

$$= -126,150 \frac{kJ}{kmol C_4 H_{10}}$$



#### TABLE A-26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at  $25^{\circ}\text{C}$ , 1 atm

		$\overline{h}_f^\circ$	$ar{g}_{\!f}^{\circ}$	<b>S</b> °
Substance	Formula	kJ/kmol	kJ/kmol	kJ/kmol · K
Carbon	C(s)	0	0	5.74
Hydrogen	H <sub>2</sub> (g)	0	0	130.68
Nitrogen	$N_2(g)$	0	0	191.61
Oxygen	$O_2(g)$	0	0	205.04
Carbon monoxide	CO(g)	-110,530	-137,150	197.65
Carbon dioxide	$CO_2(g)$	-393,520	-394,360	213.80
Water vapor	$H_2\bar{O}(g)$	-241,820	-228,590	188.83
Water	$H_2^{-}O(\ell)$	-285,830	-237,180	69.92
Hydrogen peroxide	$H_2^- O_2(g)$	-136,310	-105,600	232.63
Ammonia	$NH_3(g)$	-46,190	-16,590	192.33
Methane	$CH_4(g)$	-74,850	-50,790	186.16
Acetylene	$C_2H_2(g)$	+226,730	+209,170	200.85
Ethylene	$C_2H_4(g)$	+52,280	+68,120	219.83
Ethane	$C_2H_6(g)$	-84,680	-32,890	229.49
Propylene	$C_3H_6(g)$	+20,410	+62,720	266.94
Propane	$C_3H_8(g)$	-103,850	-23,490	269.91
<i>n</i> -Butane	$C_4H_{10}(g)$	-126,150	-15,710	310.12
<i>n</i> -Octane	$C_8H_{18}(g)$	-208,450	+16,530	466.73
<i>n</i> -Octane	$C_8H_{18}(\ell)$	-249,950	+6,610	360.79
<i>n</i> -Dodecane	$C_{12}H_{26}(g)$	-291,010	+50,150	622.83
Benzene	$C_6H_6(g)$	+82,930	+129,660	269.20
Methyl alcohol	CH <sub>3</sub> OH( <i>g</i> )	-200,670	-162,000	239.70
Methyl alcohol	$CH_3OH(\ell)$	-238,660	-166,360	126.80
Ethyl alcohol	$C_2H_5OH(g)$	-235,310	-168,570	282.59
Ethyl alcohol	$C_2H_5OH(\ell)$	-277,690	-174,890	160.70
Oxygen	O( <i>g</i> )	+249,190	+231,770	161.06
Hydrogen	H( <i>g</i> )	+218,000	+203,290	114.72
Nitrogen	N( <i>g</i> )	+472,650	+455,510	153.30
Hydroxyl	OH( <i>g</i> )	+39,460	+34,280	183.70

Source: From JANAF, Thermochemical Tables (Midland, MI: Dow Chemical Co., 1971); Selected Values of Chemical Thermodynamic Properties, NBS Technical Note 270-3, 1968; and API Research Project 44 (Carnegie Press, 1953).



•Products: TP = 1000 K

Comp	$N_e$	$\overline{h}_{\!f}^{o}$	$\overline{h}_{T}$		$N_e[\overline{h}_f^o + (\overline{h}_T - \overline{h}^o)]_e$
	kmol/kmol fuel	kJ/kmol	kJ/kmol	kJ/kmol	kJ/kmol fuel
CO <sub>2</sub>	4	-393,520	42,769	9,364	-1,440,460
H <sub>2</sub> O	5	-241,820	35,882	9,904	-1,079,210
$N_2$	24.44	0	30,129	8,669	+524,482



#### TABLE A-18

T	$\overline{h}$	$\overline{u}$	<u></u> $ \overline{S} $	T	$\overline{h}$	$\overline{u}$	$\overline{\mathcal{S}}^{\circ}$
K	kJ/kmol	kJ/kmol	kJ/kmol · K	K	kJ/kmol	kJ/kmol	kJ/kmol · K
0	0	0	0	600	17,563	12,574	212.066
220	6,391	4,562	182.639	610	17,864	12,792	212.564
230	6,683	4,770	183.938	620	18,166	13,011	213.055
240	6,975	4,979	185.180	630	18,468	13,230	213.541
250	7,266	5,188	186.370	640	18,772	13,450	214.018
260	7,558	5,396	187.514	650	19,075	13,671	214.489
270	7,849	5,604	188.614	660	19,380	13,892	214.954
280	8,141	5,813	189.673	670	19,685	14,114	215.413
290	8,432	6,021	190.695	680	19,991	14,337	215.866
298	8,669	6,190	191.502	690	20,297	14,560	216.314
300	8,723	6,229	191.682	700	20,604	14,784	216.756
310	9,014	6,437	192.638	710	20,912	15,008	217.192
320	9,306	6,645	193.562	720	21,220	15,234	217.624
330	9,597	6,853	194.459	730	21,529	15,460	218.059
340	9,888	7,061	195.328	740	21,839	15,686	218.472
350	10,180	7,270	196.173	750	22,149	15,913	218.889
360	10,471	7,478	196.995	760	22,460	16,141	219.301
370	10,763	7,687	197.794	770	22,772	16,370	219.709
380	11,055	7,895	198.572	780	23,085	16,599	220.113
390	11,347	8,104	199.331	790	23,398	16,830	220.512
400	11,640	8,314	200.071	800	23,714	17,061	220.907
410	11,932	8,523	200.794	810	24,027	17,292	221.298
420	12,225	8,733	201.499	820	24,342	17,524	221.684
430	12,518	8,943	202.189	830	24,658	17,757	222.067
440	12,811	9,153	202.863	840	24,974	17,990	222.447
450	13,105	9,363	203.523	850	25,292	18,224	222.822
460	13,399	9,574	204.170	860	25,610	18,459	223.194
470	13,693	9,786	204.803	870	25,928	18,695	223.562
480	13,988	9,997	205.424	880	26,248	18,931	223.927
490	14,285	10,210	206.033	890	26,568	19,168	224.288
500	14,581	10,423	206.630	900	26,890	19,407	224.647
510	14,876	10,635	207.216	910	27,210	19,644	225.002
520	15,172	10,848	207.792	920	27,532	19,883	225.353
530	15,469	11,062	208.358	930	27,854	20,122	225.701
540	15,766	11,277	208.914	940	28,178	20,362	226.047
550	16,064	11,492	209.461	950	28,501	20,603	226.389
560	16,363	11,707	209.999	960	28,826	20,844	226.728
570	16,662	11,923	210.528	970	29,151	21,086	227.064
580	16,962	12,139	211.049	980	29,476	21,328	227.398
590	17,262	12,356	211.562	990	29,803	21,571	227.728





Ideal-gas properties of nitrogen, N<sub>2</sub> (Concluded)

T	$\overline{h}$	$\overline{u}$	₹°	T	$\overline{h}$	$\overline{u}$	₹°
K	kJ/kmol	kJ/kmol	kJ/kmol · K	K	kJ/kmol	kJ/kmol	kJ/kmol · K
1000	30,129	21,815	228.057	1760	56,227	41,594	247.396
1020	30,784	22,304	228.706	1780	56,938	42,139	247.798
1040	31,442	22,795	229.344	1800	57,651	42,685	248.195
1060	32,101	23,288	229.973	1820	58,363	43,231	248.589
1080	32,762	23,782	230.591	1840	59,075	43,777	248.979
1100	33,426	24,280	231.199	1860	59,790	44,324	249.365
1120	34,092	24,780	231.799	1880	60,504	44,873	249.748
1140	34,760	25,282	232.391	1900	61,220	45,423	250.128
1160	35,430	25,786	232.973	1920	61,936	45,973	250.52
1180	36,104	26,291	233.549	1940	62,654	46,524	250.874
1200	36,777	26,799	234.115	1960	63,381	47,075	251.242
1220	37,452	27,308	234.673	1980	64,090	47,627	251.607
1240	38,129	27,819	235.223	2000	64,810	48,181	251.969
1260	38,807	28,331	235.766	2050	66,612	49,567	252.858
1280	39,488	28,845	236.302	2100	68,417	50,957	253.726
1300	40,170	29,361	236.831	2150	70,226	52,351	254.578
1320	40,853	29,378	237.353	2200	72,040	53,749	255.412
1340	41,539	30,398	237.867	2250	73,856	55,149	256.227
1360	42,227	30,919	238.376	2300	75,676	56,553	257.027
1380	42,915	31,441	238.878	2350	77,496	57,958	257.810
1400	43,605	31,964	239.375	2400	79,320	59,366	258.580
1420	44,295	32,489	239.865	2450	81,149	60,779	259.332
1440	44,988	33,014	240.350	2500	82,981	62,195	260.073
1460	45,682	33,543	240.827	2550	84,814	63,613	260.799
1480	46,377	34,071	241.301	2600	86,650	65,033	261.512
1500	47,073	34,601	241.768	2650	88,488	66,455	262.213
1520	47,771	35,133	242.228	2700	90,328	67,880	262.902
1540	48,470	35,665	242.685	2750	92,171	69,306	263.577
1560	49,168	36,197	243.137	2800	94,014	70,734	264.241
1580	49,869	36,732	243.585	2850	95,859	72,163	264.895
1600	50,571	37,268	244.028	2900	97,705	73,593	265.538
1620	51,275	37,806	244.464	2950	99,556	75,028	266.170
1640	51,980	38,344	244.896	3000	101,407	76,464	266.793
1660	52,686	38,884	245.324	3050	103,260	77,902	267.404
1680	53,393	39,424	245.747	3100	105,115	79,341	268.007
1700	54,099	39,965	246.166	3150	106,972	80,782	268.601
1720	54,807	40,507	246.580	3200	108,830	82,224	269.186
1740	55,516	41,049	246.990	3250	110,690	83,668	269.763

Source: Tables A-18 through A-25 are adapted from Kenneth Wark, *Thermodynamics*, 4th ed. (New York: McGraw-Hill, 1983), pp. 787–98. Originally published in JANAF, *Thermochemical Tables*, NSRDS-NBS-37, 1971.



$$H_P = \sum_{Products} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e$$

$$= -1,995,188 \frac{kJ}{kmol \, C_4 H_{10}}$$

$$Q_{net} = H_P - H_R$$

$$= -1,869,038 \frac{kJ}{kmol \, C_4 H_{10}}$$



# Enthalpy of formation $(h_{f,i}^0)_{T_{ref}}$



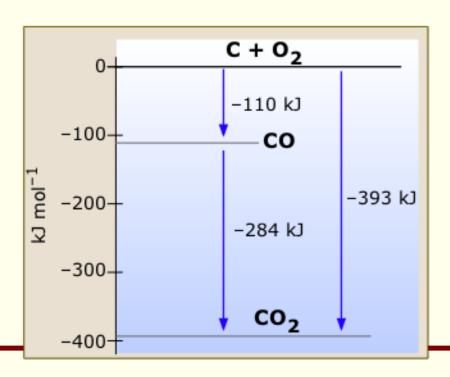
Energy/Heat Chemical reactions

Energy associated with chemical bonds or lack thereoff

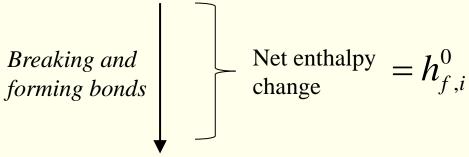


Reference state: T = 298 K, P = 1 atm

 $h_{f,i}^{o}(T_{ref})$  for elements in their naturally occurring states at reference state is 0 kJ/mol.



#### Standard State elements



### New compound of interest

$$h_{f,CO}^{0} = -110 \text{ kJ / mol}$$
  
 $h_{f,CO}^{0} = -393 \text{ kJ / mol}$ 



$$ar{h_i}(T)$$

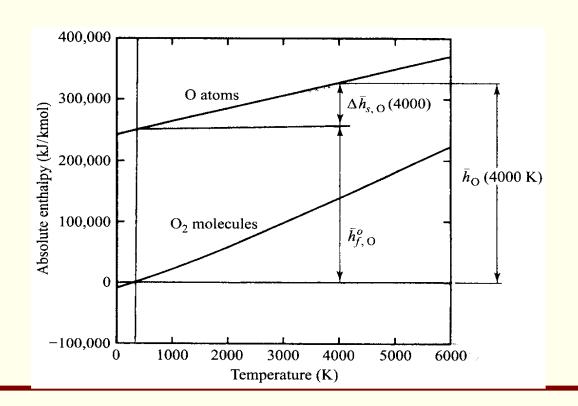
Absolute enthalpy at temperature T

$$ar{h}^o_{f,i}(T_{\mathrm{ref}})$$

Enthalpy of formation at standard reference state  $(T_{ref}, P^o)$ 

Sensible enthalpy change in going from  $T_{\text{ref}}$  to T

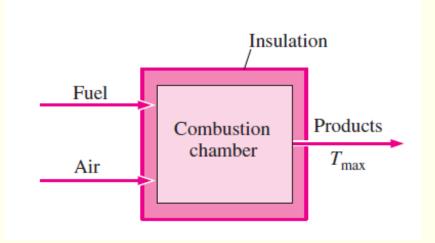
 $\Delta \bar{h}_{s,i}(T_{\rm ref}),$ 



$$\Delta \overline{h}_{s,i}(T_{ref}) = \int_{T_{ref}}^{T} \overline{C}_{p,i} dT$$



- During any reaction, the chemical energy released during a combustion process either is lost as heat to the surroundings or is used internally to raise the temperature of the combustion products.
- •The temperature, the products have when a combustion process takes place adiabatically, is called the Adiabatic flame or combustion temperature.



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



- Determination of the adiabatic flame temperature requires the use of an iterative technique.
- A temperature is assumed for the product gases, and the  $H_{prod}$  is determined for this temperature.

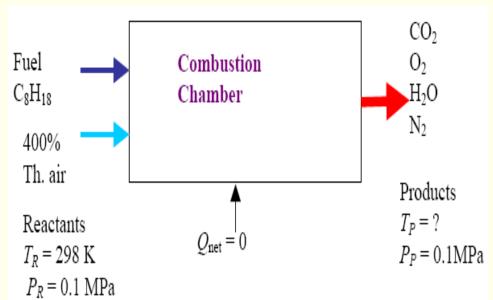


## Adiabatic flame temperature – Problem statement

• Liquid octane C8H18(liq) is burned with 400 % theoretical air. Find the adiabatic flame temperature when the reactants enter at 298 K, 0.1 MPa, and the products leave at 0.1MPa.

$$C_8H_{18} + 4(12.5) (O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 37.5 O_2 + 9 H_2 O + 188 N_2$$





• The combustion equation is

$$C_8H_{18} + 4(12.5) (O_2 + 3.76 N_2) \rightarrow 8CO_2 + 37.5 O_2 + 9H_2O + 188 N_2$$



•The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$

$$= \sum_{Products} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{Reactants} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$

$$= 0$$
 (Adiabatic Combustion)

•Thus, HP = HR for adiabatic combustion. Solve this equation for TP.



•Since the temperature of the reactants is 298 K,  $(\bar{h}_T - \bar{h}^\circ)_i = 0$ 

$$H_R = \sum_{Reactants} N_i \, \bar{h}_{fi}^o$$

$$C_8H_{18} + 4(12.5) (O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 37.5 O_2 + 9 H_2O + 188 N_2$$

$$= 1(-249,950) + 4(12.5)(0) + 4(12.5)(3.76)(0)$$

$$= -249,950 \frac{kJ}{kmol \, C_4 H_{10}}$$



$$C_{8}H_{18} + 4(12.5) (O_{2} + 3.76 N_{2}) \rightarrow 8CO_{2} + 37.5 O_{2} + 9H_{2}O + 188 N_{2}$$

$$H_{P} = \sum_{Products} N_{e} [\bar{h}_{f}^{o} + (\bar{h}_{TP} - \bar{h}^{o})]_{e}$$

$$= 8(-393,520 + \bar{h}_{TP} - 9364)_{CO_{2}} + 37.5(0 + \bar{h}_{TP} - 8682)_{O_{2}}$$

$$+9(-241,820 + \bar{h}_{TP} - 9904)_{H_{2}O} + 188(0 + \bar{h}_{TP} - 8669)_{N_{2}}$$

$$= (-7,443,845 + 8\bar{h}_{TP,CO_{2}} + 9\bar{h}_{TP,H_{2}O} + 37.5\bar{h}_{TP,O_{2}} + 188\bar{h}_{TP,N_{2}})_{\frac{kJ}{kmol C_{4}H_{10}}}$$



•Thus, setting  $H_P = H_R$  yields

$$\sum_{\text{Products}} N_e \bar{h}_{T_P, e} = 8 \bar{h}_{T_P, CO_2} + 9 \bar{h}_{T_P, H_2O} + 37.5 \bar{h}_{T_P, O_2} + 188 \bar{h}_{T_P, N_2}$$

$$= 7,193,895$$

•To estimate TP, assume all products behave like  $N_2$  and estimate the adiabatic flame temperature from the nitrogen data.



$$242.5\overline{h}_{T_P, N_2} = 7,193,895$$

$$\bar{h}_{T_P, N_2} = 29,665.5 \frac{kJ}{kmol \ N_2}$$

$$T_p \cong 985 K$$

•Because  $CO_2$  and  $H_2O$  are triatomic gases and have specific heats greater than diatomic gases, the actual temperature will be somewhat less than 985 K. Try TP = 960 K and 970K.

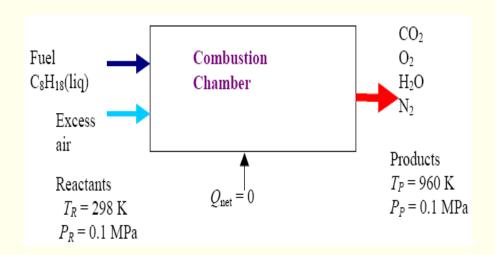


	$N_e$	$\overline{h}_{960\ K}$	$\overline{h}_{970\ K}$
$CO_2$	8	40,607	41,145
H <sub>2</sub> O	9	34,274	34,653
$O_2$	37.5	29,991	30,345
$N_2$	188	28,826	29,151
F	$\sum_{Produts} N_e \overline{h}_{T_P,\epsilon}$	7,177,572	7,259,362

• Interpolation gives: TP = 962 K.



# Adiabatic flame temperature – problem



•Liquid octane C<sub>8</sub>H<sub>18</sub>(liq) is burned with excess air. The adiabatic flame temperature is 960 K when the reactants enter at 298 K, 0.1 MPa, and the products leave at 0.1MPa. What percent excess air is supplied?



## Calculate % Excess Air for given Tp

•Let A be the excess air; then combustion equation is

$$C_8H_{18} + (1+A)(12.5) (O_2 + 3.76 N_2) \rightarrow$$
  
8  $CO_2 + 12.5A O_2 + 9 H_2O + (1+A)(12.5)(3.76) N_2$ 

•The steady-flow heat transfer is

$$Q_{net} = H_P - H_R = 0$$
 (Adiabatic Combustion)

$$= \sum_{Products} N_e [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{Reactants} N_i [\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$



# Calculate % Excess Air for given Tp

- •Here, since the temperatures are known, the values of  $\overline{h}_{T_P}$  are known.
- •The product gas mole numbers are unknown but are functions of the amount of excess air, A.
- The energy balance can be solved for A.

$$A = 3$$

•Thus, 300 percent excess, or 400 percent theoretical, air is supplied.



# Calculate % Excess Air for given Tp

- •Tabulate the adiabatic flame temperature as a function of excess air for the complete combustion of C<sub>3</sub>H<sub>8</sub> when the fuel enters the steady-flow reaction chamber at 298 K and the air enters at 400 K.
- •The combustion equation is:

$$C_3H_8 + (1+A)(5)(O_2 + 3.76N_2) \rightarrow$$
  
  $3CO_2 + 5AO_2 + 4H_2O + (1+A)(5)(3.76)N_2$ 

where A is the value of excess air in decimal form.



#### Calculate % Excess Air for given Tp

•The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$

$$= \sum_{P} N_{e} [\, \bar{h}_{f}^{o} + (\bar{h}_{T} - \bar{h}^{o})]_{e} - \sum_{R} N_{i} [\, \bar{h}_{f}^{o} + (\bar{h}_{T} - \bar{h}^{o})]_{i}$$

= 0 (Adiabatic combustion)



### Calculate % Excess Air for given Tp

% Excess Air	Adiabatic Flame Temp. (K)		
0	2459.3		
20	2191.9		
50	1902.5		
100	1587.1		
217	1200		

• The adiabatic flame temperature decreases as a result of incomplete combustion or using excess air. Also, the maximum adiabatic flame temperature is achieved when complete combustion occurs with the theoretical amount of air.



# Adiabatic flame temperature

- The adiabatic flame temperature of a fuel is not unique. Its value depends on :
  - (1) the state of the reactants,
  - (2) the degree of completion of the reaction, and
  - (3) the amount of air used.
- For a specified fuel at a specified state burned with air at a specified state, the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air.



Theoretical temperature of reaction products if no heat is lost to the surroundings

Depending on the combustion system:

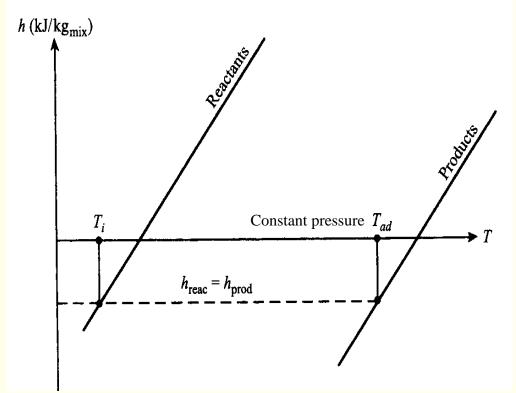
- Constant pressure  $T_{ad}$
- Constant volume  $T_{ad}$

#### Focus on constant Pressure $T_{ad}$

If a fuel—air mixture burns adiabatically at constant pressure, on applying the **first law of thermodynamics** we see that the standardized enthalpy of the reactants at the initial state (say, T = 298 K, P = 1 atm) equals the standardized enthalpy of the products at the final state ( $T = T_{ad}$ , P = 1 atm)



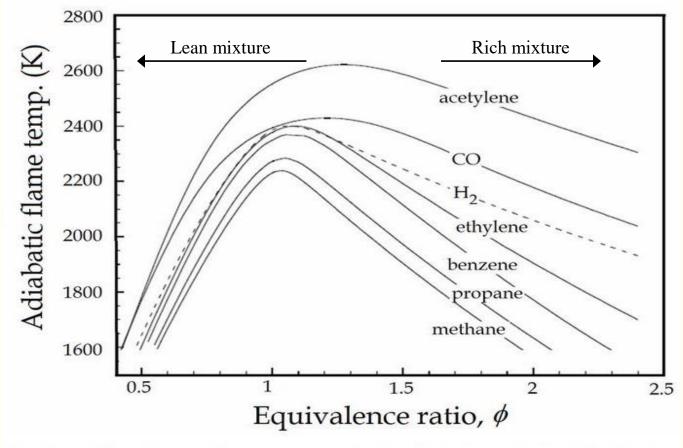
# Constant pressure $T_{ad}$



Fuel	Oxidizer	Constant pressure $T_{ad}$ (°C)	
Methane	Air	1950	
Ethane	Air	1955	
Natural gas	Air	1960	
Butane	Air	1970	
Wood	Air	1980	
Propane	Air	1980	

Conceptually very simple but requires knowledge of product composition. Products may contain many species

# Constant pressure $T_{ad}$

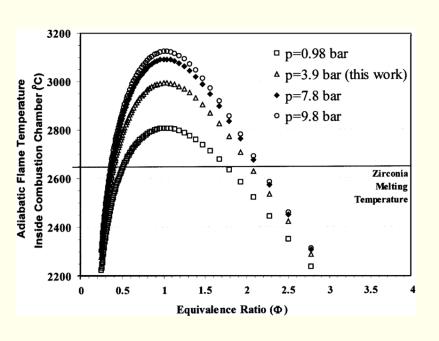


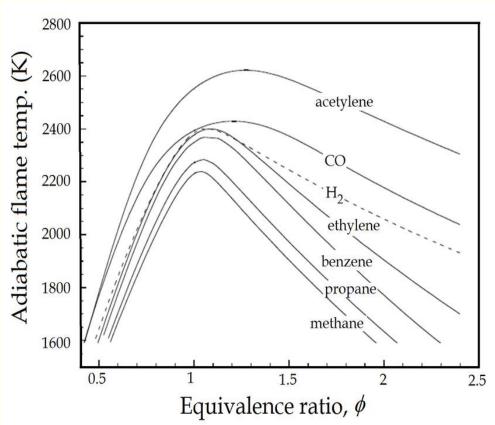
The adiabatic flame temperature as a function of the equivalence ratio for various fuel-air mixtures at STP. Reproduced from Reference [10] with permission (Copyright Cambridge University Press 2006).

The equivalence ratio is defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio.



# T<sub>Ad</sub>







### **Enthalpy of Reaction and Enthalpy of Combustion**

- •When the products and reactants are at the same temperature, the enthalpy of reaction  $h_R$ , is the difference in their enthalpies.
- •When the combustion is assumed to be complete with theoretical air supplied, the enthalpy of reaction is called the enthalpy of combustion  $h_C$ .



### **Enthalpy of Combustion**

•The enthalpy of combustion can be calculated at any value of the temperature, but it is usually determined at 25°C or 298 K.

$$\bar{h}_C = H_P - H_R$$
 when  $T_P = T_R = 25^{\circ}C = 298 \, K$ 

$$\sum_{Products} N_e \, \bar{h}_{fe}^o - \sum_{Reactants} N_i \, \bar{h}_{fi}^o$$



## **Heating value**

•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, HV, of a fuel is the absolute value of the enthalpy of combustion. (kJ/kg of fuel)

$$HV = |\bar{h}_C|$$

• HV depends on the *phase* of the H<sub>2</sub>O in the products.

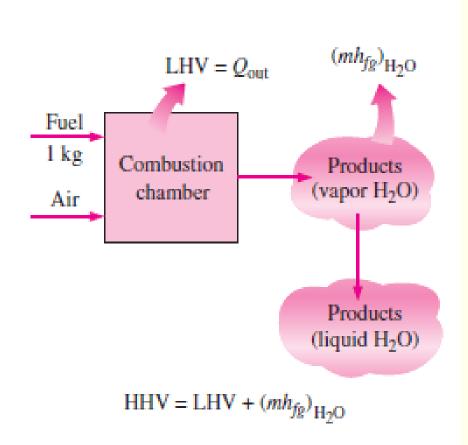


### **Heating Value**

- •The heating value is called the **higher heating value** (HHV) when the H<sub>2</sub>O in the products is in the liquid form, and it is called the **lower heating value** (LHV) when the H<sub>2</sub>O in the products is in the vapor form.
- $HHV = |\bar{h}_C| = -\bar{h}_C$  with  $H_2O_{liquid}$  in products
- The lower heating value, LHV, is the heating value when water appears as a gas in the products.
- $LHV = |\bar{h}_C| = -\bar{h}_C$  with  $H_2O_{vapour}$  in products



#### **HHV** and **LHV**



• The heating value or enthalpy of combustion of a fuel can be determined from a knowledge of the enthalpy of formation for the compounds involved



#### **HHV** and **LHV**

- Heating values of fuels are available at 25 °C and are given in kJ/kg of fuel. One has to multiply the same by the molar mass of the fuel to determine the heating value in units of kJ/kmol of fuel.
- The higher and lower heating values are related by the amount of water formed during the combustion process and the enthalpy of vaporization of water at the temperature.

$$HHV = LHV + N_{H_2O}\overline{h}_{fg\,H_2O}$$

#### TABLE A-27

Properties of some common fuels and hydrocarbons

Fuel (phase)	Formula	Molar mass, kg/kmol	Density, <sup>1</sup> kg/L	Enthalpy of vaporization, <sup>2</sup> kJ/kg	Specific heat, $c_p$ kJ/kg · K	Higher heating value, <sup>3</sup> kJ/kg	Lower heating value, <sup>3</sup> kJ/kg
Carbon (s)	С	12.011	2	_	0.708	32,800	32,800
Hydrogen (g)	$H_2$	2.016	_	_	14.4	141,800	120,000
Carbon monoxide (g)	CO	28.013	_	_	1.05	10,100	10,100
Methane (g)	CH₄	16.043		509	2.20	55,530	50,050
Methanol $(\ell)$	CH <sub>4</sub> O	32.042	0.790	1168	2.53	22,660	19,920
Acetylene (g)	$C_2H_2$	26.038	_	_	1.69	49,970	48,280
Ethane (g)	$C_2H_6$	30.070	_	172	1.75	51,900	47,520
Ethanol ( $\ell$ )	$C_2H_6O$	46.069	0.790	919	2.44	29,670	26,810
Propane ( $\ell$ )	$C_3H_8$	44.097	0.500	335	2.77	50,330	46,340
Butane (ℓ)	$C_4H_{10}$	58.123	0.579	362	2.42	49,150	45,370
1-Pentene (ℓ)	$C_5H_{10}$	70.134	0.641	363	2.20	47,760	44,630
Isopentane ( $\ell$ )	$C_5H_{12}$	72.150	0.626	_	2.32	48,570	44,910
Benzene (ℓ)	$C_6H_6$	78.114	0.877	433	1.72	41,800	40,100
Hexene (ℓ)	$C_6H_{12}$	84.161	0.673	392	1.84	47,500	44,400
Hexane (ℓ)	$C_6H_{14}$	86.177	0.660	366	2.27	48,310	44,740
Toluene ( $\ell$ )	C <sub>7</sub> H <sub>8</sub>	92.141	0.867	412	1.71	42,400	40,500
Heptane (ℓ)	$C_7H_{16}$	100.204	0.684	365	2.24	48,100	44,600
Octane ( $\ell$ )	C <sub>8</sub> H <sub>18</sub>	114.231	0.703	363	2.23	47,890	44,430
Decane (ℓ)	$C_{10}H_{22}$	142.285	0.730	361	2.21	47,640	44,240
Gasoline ( $\ell$ )	$C_n H_{1.87n}$	100-110	0.72-0.78	350	2.4	47,300	44,000
Light diesel ( $\ell$ )	$C_nH_{1.8n}$	170	0.78-0.84	270	2.2	46,100	43,200
Heavy diesel ( $\ell$ )	$C_nH_{1.7n}$	200	0.82-0.88	230	1.9	45,500	42,800
Natural gas (g)	$C_n H_{3.8n} N_{0.1n}$	18	_	_	2	50,000	45,000

<sup>&</sup>lt;sup>1</sup>At 1 atm and 20°C.

 $<sup>^2\</sup>mbox{At }25\mbox{\,}^{\circ}\mbox{C}$  for liquid fuels, and 1 atm and normal boiling temperature for gaseous fuels.

 $<sup>^3\</sup>mbox{At }25\mbox{\,}^{\circ}\mbox{C}.$  Multiply by molar mass to obtain heating values in kJ/kmol.



#### **HHV and LHV - problem**

•The enthalpy of combustion of gaseous octane  $C_8H_{18}$  at 25 °C with liquid water in the products is -5,500,842 kJ/kmol. Find the lower heating value of liquid octane.

$$\begin{split} LHV_{C_8H_{18}\ gas} &= HHV_{C_8H_{18}\ liq} - N_{H_2O}\bar{h}_{fg\ H_2O} \\ &= 5,500,842 \frac{kJ}{kmol\ C_8H_{18}} - 9\frac{kmol\ H_2O}{kmol\ C_8H_{18}} (44,010) \frac{kJ}{kmol\ H_2O} \\ &= 5,104,752 \frac{kJ}{kmol\ C_8H_{18}} \end{split}$$



### **HHV and LHV - problem**

$$LHV_{C_8H_{18\ liq}} = LHV_{C_8H_{18\ gas}} - \overline{h}_{fg\ C_8H_{18}}$$

$$= (5,104752 - 41,382) \frac{kJ}{kmol\ C_8 H_{18}}$$

$$= 5,063,370 \frac{kJ}{kmol \ C_8 H_{18 \ liq}}$$

•Can you explain why LHVliq < LHVgas?



# **Closed System**

•Apply the first law closed system:

$$E_{in} - E_{out} = \Delta E$$

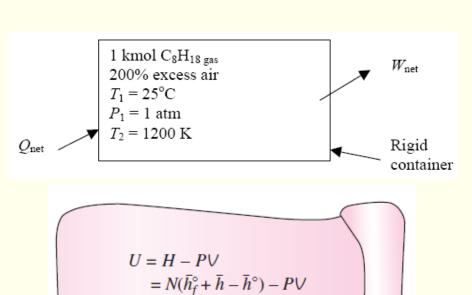
$$Q_{net} - W_{net} = U_P - U_R$$

• In order to avoid another term  $U_f^0$ , we can use Enthalpy.

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

• The Pv- terms are negligible for solids and liquids, and can be replaced by  $R_uT$  for gases that behave as an ideal gas.

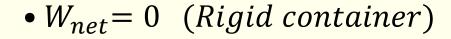


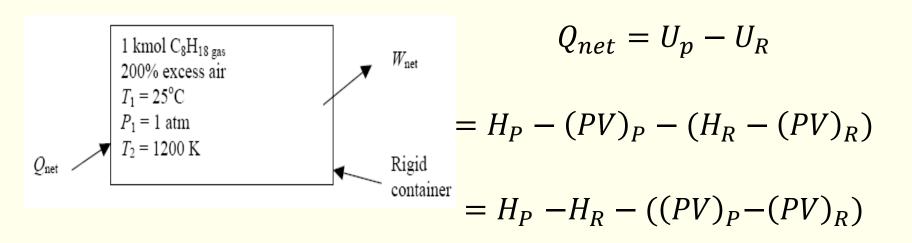


 $= N(\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ} - P\bar{v})$ 

•A mixture of 1 kmol C<sub>8</sub>H<sub>18</sub> gas and 200 percent excess air at 25 °C, 1 atm, is burned completely in a closed system (a bomb) and is cooled to 1200 K. Find the heat transfer from the system and the system final pressure.









Assume that the reactants and products are ideal gases; then

$$PV = NR_uT$$

$$Q_{net} = H_P - H_R - \left[ \sum_{Products} N_e R_u T_e - \sum_{Reactants} N_i R_i T_i \right]$$

$$= \sum_{Products} N_{e} \left[ \bar{h}_{f}^{\circ} + (\bar{h}_{T} - \bar{h}^{\circ}) - R_{u} T \right]_{e}$$
$$- \sum_{Reactants} N_{i} \left[ \bar{h}_{f}^{\circ} + (\bar{h}_{T} - \bar{h}^{\circ}) - R_{u} T \right]_{i}$$



•The balanced combustion equation for 200 percent excess (300 percent theoretical) air is

$$C_8H_{18} + (3)(12.5) (O_2 + 3.76 N_2) \rightarrow 8 CO_2 + 25 O_2 + 9 H_2O + 141 N_2$$

$$Q_{net} = 8(-393,520 + 53,848 - 9364 - 8.314(1200))_{CO_2}$$

$$+9(-241,820 + 44,380 - 9904 - 8.314(1200))_{H_2O}$$

$$+25(0 + 38,447 - 8682 - 8.314(1200))_{O_2}$$

$$+141(0 + 36,777 - 8669 - 8.314(1200))_{N_2}$$



$$-1(-208,450 + \bar{h}_{298K} - \bar{h}^o - 8.314(298)))_{C_8H_{18}}$$

$$-37.5(0 + 8682 - 8682 - 8.314(298)))_{O_2}$$

$$-141(0 + 8669 - 8669 - 8.314(298)))_{N_2}$$

$$= -1.12 \cdot 10^6 \frac{kJ}{kmol \ C_8H_{18}}$$



•To find the final pressure, assume that the reactants and the products are ideal-gas mixtures.

$$P_1 V_1 = N_1 R_u T_1$$

$$P_2V_2 = N_2R_uT_2$$

•where state 1 is the state of the mixture of the reactants before the combustion process and state 2 is the state of the mixture of the products after the combustion process takes place.

•Note that the total moles of reactants are not equal to the total moles of products.



$$\frac{P_2 V_2}{P_1 V_1} = \frac{N_2 R_u T_2}{N_1 R_u T_1}$$

• but  $V_2 = V_1$ .

$$P_2 = P_1 \frac{N_2}{N_1} \frac{T_2}{T_1}$$

$$= 1atm \left(\frac{183 \ kmol \ products}{179.5 \ kmol \ reactants}\right) \left(\frac{1200 K}{298 K}\right)$$

4.11 atm



#### **Problem**

•Liquid propane (C3H8) enters a combustion chamber at 25°C at a rate of 0.05 kg/min where it is mixed and burned with 50 percent 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 H2O but only 90 percent of the carbon burns to CO2, with the remaining 10 percent forming CO. If the exit temperature of the combustion gases is 1500 K, determine (a) the mass flow rate of air and (b) the rate of heat transfer from the combustion chamber.



MF

TABLE A-21

Ideal-gas properties of carbon monoxide, CO (Concluded)

T	<del>h</del>	$\overline{u}$	$\overline{s}^{\circ}$	T	<del>h</del>	$\overline{u}$	ō°
K	kJ/kmol	kJ/kmol	kJ/kmol · K	K	kJ/kmol	kJ/kmol	kJ/kmol · K
1000	30,355	22,041	234.421	1760	56,756	42,123	253.991
1020	31,020	22,540	235.079	1780	57,473	42,673	254.398
1040	31,688	23,041	235.728	1800	58,191	43,225	254.797
1060	32,357	23,544	236.364	1820	58,910	43,778	255.194
1080	33,029	24,049	236.992	1840	59,629	44,331	255.587
1100	33,702	24,557	237.609	1860	60,351	44,886	255.976
1120	34,377	25,065	238.217	1880	61,072	45,441	256.361
1140	35,054	25,575	238.817	1900	61,794	45,997	256.743
1160	35,733	26,088	239.407	1920	62,516	46,552	257.122
1180	36,406	26,602	239.989	1940	63,238	47,108	257.497
1200	37,095	27,118	240.663	1960	63,961	47,665	257.868
1220	37,780	27,637	241.128	1980	64,684	48,221	258.236
1240	38,466	28,426	241.686	2000	65,408	48,780	258.600
1260	39,154	28,678	242.236	2050	67,224	50,179	259.494
1280	39,844	29,201	242.780	2100	69,044	51,584	260.370
1300	40,534	29,725	243.316	2150	70,864	52,988	261.226
1320	41,226	30,251	243.844	2200	72,688	54,396	262.065
1340	41,919	30,778	244.366	2250	74,516	55,809	262.887
1360	42,613	31,306	244.880	2300	76,345	57,222	263.692
1380	43,309	31,836	245.388	2350	78,178	58,640	264.480
1400	44,007	32,367	245.889	2400	80,015	60,060	265.253
1420	44,707	32,900	246.385	2450	81,852	61,482	266.012
1440	45,408	33,434	246.876	2500	83,692	62,906	266.755
1460	46,110	33,971	247.360	2550	85,537	64,335	267.485
1480	46,813	34,508	247.839	2600	87,383	65,766	268.202
1500	47,517	35,046	248.312	2650	89,230	67,197	268.905
1520	48,222	35,584	248.778	2700	91,077	68,628	269.596
1540	48,928	36,124	249.240	2750	92,930	70,066	270.285
1560	49,635	36,665	249.695	2800	94,784	71,504	270.943
1580	50,344	37,207	250.147	2850	96,639	72,945	271.602
1600	51,053	37,750	250.592	2900	98,495	74,383	272.249
1620	51,763	38,293	251.033	2950	100,352	75,825	272.884
1640	52,472	38,837	251.470	3000	102,210	77,267	273.508
1660	53,184	39,382	251.901	3050	104,073	78,715	274.123
1680	53,895	39,927	252.329	3100	105,939	80,164	274.730
1700	54,609	40,474	252.751	3150	107,802	81,612	275.326
1720	55,323	41,023	253.169	3200	109,667	83,061	275.914
1740	56,039	41,572	253.582	3250	111,534	84,513	276.494



#### TABLE A-26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at  $25^{\circ}\text{C}$ , 1 atm

		$\overline{h}_f^\circ$	$ar{g}_{\!f}^{\circ}$	<u>S</u> °
Substance	Formula	kJ/kmol	kJ/kmol	kJ/kmol · K
Carbon	C(s)	0	0	5.74
Hydrogen	H <sub>2</sub> (g)	0	0	130.68
Nitrogen	$N_2(g)$	0	0	191.61
Oxygen	$O_2(g)$	0	0	205.04
Carbon monoxide	CO(g)	-110,530	-137,150	197.65
Carbon dioxide	$CO_2(g)$	-393,520	-394,360	213.80
Water vapor	$H_2\bar{O}(g)$	-241,820	-228,590	188.83
Water	$H_2^{-}O(\ell)$	-285,830	-237,180	69.92
Hydrogen peroxide	$H_2^- O_2(g)$	-136,310	-105,600	232.63
Ammonia	$NH_3(g)$	-46,190	-16,590	192.33
Methane	$CH_4(g)$	-74,850	-50,790	186.16
Acetylene	$C_2H_2(g)$	+226,730	+209,170	200.85
Ethylene	$C_2H_4(g)$	+52,280	+68,120	219.83
Ethane	$C_2H_6(g)$	-84,680	-32,890	229.49
Propylene	$C_3H_6(g)$	+20,410	+62,720	266.94
Propane	$C_3H_8(g)$	-103,850	-23,490	269.91
<i>n</i> -Butane	$C_4H_{10}(g)$	-126,150	-15,710	310.12
<i>n</i> -Octane	$C_8H_{18}(g)$	-208,450	+16,530	466.73
<i>n</i> -Octane	$C_8H_{18}(\ell)$	-249,950	+6,610	360.79
<i>n</i> -Dodecane	$C_{12}H_{26}(g)$	-291,010	+50,150	622.83
Benzene	$C_6H_6(g)$	+82,930	+129,660	269.20
Methyl alcohol	CH <sub>3</sub> OH( <i>g</i> )	-200,670	-162,000	239.70
Methyl alcohol	$CH_3OH(\ell)$	-238,660	-166,360	126.80
Ethyl alcohol	$C_2H_5OH(g)$	-235,310	-168,570	282.59
Ethyl alcohol	$C_2H_5OH(\ell)$	-277,690	-174,890	160.70
Oxygen	O( <i>g</i> )	+249,190	+231,770	161.06
Hydrogen	H( <i>g</i> )	+218,000	+203,290	114.72
Nitrogen	N( <i>g</i> )	+472,650	+455,510	153.30
Hydroxyl	OH( <i>g</i> )	+39,460	+34,280	183.70

Source: From JANAF, Thermochemical Tables (Midland, MI: Dow Chemical Co., 1971); Selected Values of Chemical Thermodynamic Properties, NBS Technical Note 270-3, 1968; and API Research Project 44 (Carnegie Press, 1953).