Air Pollution and GHGs

Chapter 3 – Gas Combustion Basics

Combustion

- Combustion is NOT the scope of this chapter; **air emission** is.
- O_2+ Fuel → Wanted energy + Unwanted emissions

Air-Fuel Ratio, A/F

- In combustion analysis, the relative quantity of air and fuel in the combustion mixture is needed,
- a term of air-fuel ratio is defined to assist in this analysis.
- **air-fuel ratio** (A/F) is the ratio of air to fuel present in mixture of reactants for combustion.

$$n_a A + n_f F \rightarrow n_p P$$

Air-Fuel Ratios

$$n_a A + n_f F \rightarrow n_p P$$

- **Air-fuel mole ratio,**

$$(A/F)_v = \frac{n_a}{n_f} = \frac{\left(\sum n_i\right)_{air}}{\left(\sum n_i\right)_{fuel}}$$

- Air-fuel mass ratio

$$(A/F)_m = \frac{m_{air}}{m_{fuel}} = \frac{\left(\sum n_i M_i\right)_{air}}{\left(\sum n_i M_i\right)_{fuel}}$$

  - These two values are different
  - Mole ratio by default unless stated otherwise

Air-Fuel Mixtures

- **Stoichiometric mixture:**
  - all the fuel is combined with all of the free oxygen, the mixture is chemically balanced
- **Fuel lean mixture**:
  - more air than needed to completely burn the fuel in the mixture
  - less air emissions
- **Fuel rich mixture:**
  - Incomplete combustion
  - More air emissions

Equivalence Ratio

Stoichiometric

$$\phi = \frac{(A/F)_s}{(A/F)_{mix}}$$

- Dimensionless variable
  - Φ=1 → Stoichiometric
  - Φ>1 → Fuel rich
  - Φ<1 → Fuel lean

A/F Example

Consider a mixture of one mole of ethane (C_2H_6) and 15 moles of air. Determine,

a) the air to fuel ratio of this mixture

b) the equivalence ratio of this mixture if the stoichiometric air to fuel ratio based on mass is 16.66

Solution $(A/F)_{mix}$=15 by definition

Assuming the mixture is in the same container and reached steady state without chemical reactions. The A/F based on volume is simply

$$\phi = \frac{(A/F)_s}{(A/F)_{mix}} = \frac{16.66}{15} = 1.11$$

It is a fuel rich mixture.

Discussion

- Consider a complete combustion between 1 ton of C_3H_8 with air, how much CO_2 can be produced?
- **We need to know the chemical reaction formula first**

Combustion Stoichiometry

Combustion Stoichiometry

- If we know the composition of reactants and products, say CH_4 burnt with pure O_2 producing CO_2 and H_2O only.

$$CH_4 + aO_2 \rightarrow bCO_2 + cH_2O$$

- a=? b=? c=?

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

More general

$$C_\alpha H_\beta + aO_2 \rightarrow b\,CO_2 + cH_2O$$

Solution

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right)O_2 \rightarrow \alpha\,CO_2 + \frac{\beta}{2}H_2O$$

Generalize more by replacing O_2 with **AIR**

- 1 mole of air ~ 0.21 mole of Oxygen molecules + 0.79 moles of nitrogen molecules
- In this air, 1 mole of O_2 comes with 3.76 mole of N_2
- The number of 3.76 comes from the molar ratio of N_2 to O_2 in a dry air, which is 0.79/0.21 = 3.76.

Combustion with **air**

1Air=$0.21O_2$+$0.79N_2$

$$C_\alpha H_\beta + a(0.21O_2 + 0.79N_2) \rightarrow b\,CO_2 + cH_2O + dN_2$$

- N_2 remains unreacted at "low" temperatures
- Determine a, b, c, d

$$C_\alpha H_\beta + 4.76\left(\alpha + \frac{\beta}{4}\right)(0.21O_2 + 0.79N_2) \rightarrow \alpha\,CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4}\right)N_2$$

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2) \rightarrow \alpha\,CO_2 + \frac{\beta}{2}H_2O + 3.76\left(\alpha + \frac{\beta}{4}\right)N_2$$

The corresponding stoichiometric air/fuel ratio is

$$(A/F)_s = \frac{n_{air}}{n_{fuel}} = 4.76\left(\alpha + \frac{\beta}{4}\right)$$

Fuel-Lean Combustion

$$C_\alpha H_\beta + a(0.21O_2 + 0.79N_2) \rightarrow bCO_2 + cH_2O + dN_2 + eO_2$$

- Some left unreacted

Balance this fuel-lean combustion chemical formula in terms of α, β and ϕ

Solution

$$C_\alpha H_\beta + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2 + eO_2$$

$$\left(A/F\right)_{mix} = \frac{4.76a}{1} \Rightarrow a = \frac{(A/F)_{mix}}{4.76}$$

From the definition of the equivalence ratio, ϕ

$$\phi = \frac{\left(A/F\right)_s}{\left(A/F\right)_{mix}} \quad \Rightarrow \quad \left(A/F\right)_{mix} = \frac{\left(A/F\right)_s}{\phi}$$

$$\Rightarrow \quad a = \frac{\left(A/F\right)_s}{4.76\phi} = \frac{1}{4.76\phi}\left(\alpha + \frac{\beta}{4}\right)$$

Solution (Cont…)

$$C_\alpha H_\beta + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2 + eO_2$$

Balance of C and H:

$b = \alpha$

$c = \beta/2$

Balance of N $\Rightarrow d = \dfrac{3.76(\alpha + \beta/4)}{\phi}$

Balance of O $\Rightarrow \dfrac{2(\alpha + \beta/4)}{\phi} = 2\alpha + \dfrac{\beta}{2} + 2e$

$\Rightarrow e = \left(\dfrac{1}{\phi} - 1\right)\left(\alpha + \dfrac{\beta}{4}\right)$

Fuel lean combustion formula

$$C_\alpha H_\beta + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2)$$
$$\rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O + \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4}\right)N_2 + \left(\frac{1}{\phi} - 1\right)\left(\alpha + \frac{\beta}{4}\right)O_2$$

Comment:

- Known parameters: α, β, and ϕ (fuel formula and Equivalence Ratio)

Example

Under certain conditions, a thermochemical conversion (TCC) process produced a liquid alkane fuel that contains 80% by mass carbon and 20% by mass hydrogen.

- Determine the formula of this fuel, $C_\alpha H_\beta$

Solution

Element	Wt %	mol/100g fuel	mol/mol C
C	*80%*	*=80/12=6.67*	*1*
H	*20%*	*=20/1 =20*	*=20/6.67=3*

So the effective fuel composition = $\mathbf{CH_3}$

- If the fuel is burned with 10% excess air by volume,
  - what is the equivalence ratio of the mixture?
  - determine the chemical reaction formula.

Solution (cont…)

Step 1: *determine the* *stoichiometric* *combustion of* CH_3

$$CH_3 + (1.75)(O_2 + 3.76N_2) \rightarrow CO_2 + 1.5H_2O + 6.58N_2$$

Solution (cont…)

Step 1: Stoichiometric reaction formula

$$CH_3 + (1.75)(O_2 + 3.76N_2) \rightarrow CO_2 + 1.5H_2O + 6.58N_2$$

Step 2: *determine the* *fuel lean* *combustion of* CH_3

- *With 10% of excess air*

$$CH_3 + 1.1(1.75)(O_2 + 3.76N_2) \rightarrow CO_2 + 1.5H_2O + aO_2 + bN_2$$

You could determine a and b by O and N balances

$$CH_3 + 1.1(1.75)(O_2 + 3.76N_2) \rightarrow CO_2 + 1.5H_2O + aO_2 + bN_2$$

$$a = \frac{1}{\phi} - 1 = 0.1$$

$$b = 3.76\frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right) = 1.1 \times 1.75 \times 3.76 = 7.238$$

- **For one ton of this fuel burned with 10% of excess air, how many tons of CO_2 is produced?**

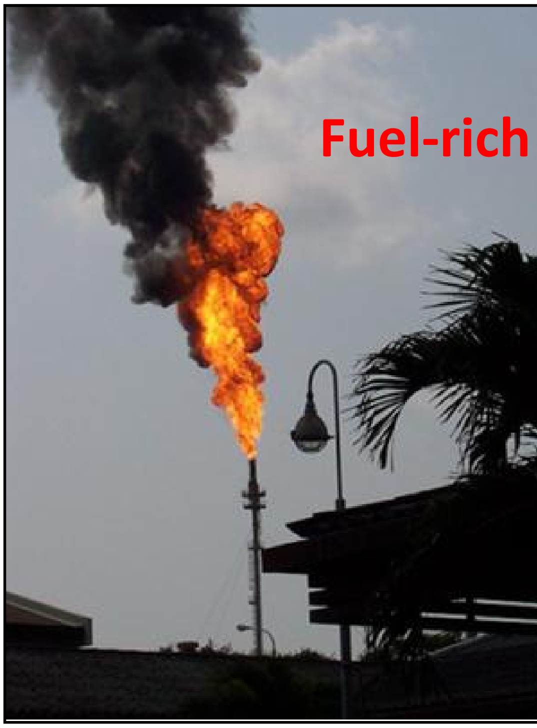
Real fuel

$C_\alpha H_\beta O_o Cl_q S_s N_n$ burn with air (fuel lean)

$$C_\alpha H_\beta O_o Cl_q S_s N_n + a(O_2 + 3.76N_2)$$
$$\rightarrow bCO_2 + cH_2O + dHCl + eN_2 + fSO_2$$

$$CH_4 + 2(O_2 + 3.76N_2)$$
$$\rightarrow aCO_2 + bCO + cH_2O + dH_2 + (2 \times 3.76)N_2$$

Calculate a, b, c, and d



Fuel-rich combustion

- More complicated.
- Requires knowledge in chemical equilibrium.

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Fuel-rich combustion

- A simple example

Reactants (mixture before ignition) $$C_\alpha H_\beta + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2)$$

Products (mixture after combustion) $$\rightarrow \left(aCO_2 + bCO\right) + cH_2O + dN_2 + eH_2$$

- Carbon is shared by CO_2 and CO
- Hydrogen is shared by H2O and H2

Can you determine this reaction formula

$$C_\alpha H_\beta + \frac{1}{\phi}\left(\alpha + \frac{\beta}{4}\right)(O_2 + 3.76N_2) \rightarrow \left(aCO_2 + bCO\right) + cH_2O + dN_2 + eH_2$$

$\alpha = a + b$

$\beta = 2c + 2e$

$$\frac{2}{\phi}\left(\alpha + \frac{\beta}{4}\right) = 2a + b + c \qquad \frac{3.76}{\phi}\left(\alpha + \frac{\beta}{4}\right) = d$$

Only *d* can be determined from the nitrogen balance.

One more equation is needed to solve the problem

Effect of

Chemical Equilibrium

on Air Emissions

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Micro and Macro Chemical Reactions

- For a general combustion reaction

Macro

$$oO + fF \rightarrow aA + bB + cC + dD + \cdots + zZ$$

Micro

$$A \leftrightarrow B + \tfrac{1}{2}C$$

$$2C + D \leftrightarrow 3X + \tfrac{1}{2}Y.$$

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Reaction constant, k

- For a general combustion reaction

$$aA + bB \overset{k}{\rightarrow} cC + dD$$

- the reaction rate in terms of the consumption of the reactant is

$$-\frac{d[A]}{dt} = k[A]^a[B]^b$$

  - The negative sign indicates that the reactants are consumed in the reaction.
  - Note: **[i]= mole concentration (mol/m^3)**

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Chemical equilibrium

- When a chemical reaction reaches equilibrium, reactants and products co-exist.
- It is not a ONE-WAY reaction

- Forward reaction

$$aA + bB \xrightarrow{k_f} cC + dD$$

- Backward reaction

$$aA + bB \xleftarrow[k_b]{} cC + dD$$

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Chemical equilibrium

$$aA + bB \longleftrightarrow cC + dD$$

- The consumption of a reactant $k_f[A]^a[B]^b$
- The production of a reactant is $k_b[C]^c[D]^d$
- At equilibrium, they equal to each other

$$k_f[A]^a[B]^b \equiv k_b[C]^c[D]^d$$

Define chemical equilibrium constant, K_e

$$K_e = \frac{k_f}{k_b}$$

in terms of mole concentrations

$$K_e = \frac{k_f}{k_b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

Partial Pressure Based
Chemical equilibrium constant

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

y_i is the molar fraction of the ith species in the equilibrium mixture

$$K_P = \frac{y_C^c y_D^d}{y_A^a y_B^b}(P)^{c+d-a-b}$$

Unit of K_P: $[atm]^{(c+d)-(a+b)}$

$$K_P = \frac{n_C^c n_D^d}{n_A^a n_B^b}\left(\frac{P}{n}\right)^{c+d-a-b}$$

$$n \geq (n_A + n_B + n_C + n_D)$$

Chemical Equilibrium Example

- Consider a mixture with known amount of SO_2, SO_3 and O_2 mixed with nitrogen in a closed reactor reached chemical equilibrium at a temperature of T and a pressure of P= 2 atm. Nitrogen is assumed to be inert and does not participate in the chemical reaction. From thermodynamic literature, the equilibrium constants at 298 K and 1000 K are 2.6 x 10^{12} and 1.8, respectively.

Solution

$SO_2 + \frac{1}{2}O_2 \leftrightarrow SO_3$

- Before combustion, the n_{SO2}=1 kmole, n_{O2}=1 kmole, n_{N2}=2 kmole, after the reaction reaches equilibrium,

- Assume there is *y* kmole of SO_3, we can determine the molar amount of other gases by element balance. we can determine the molar amount of other gases by element balance.

Species	n_{SO2}	n_{O2}	n_{SO3}	n_{N2}	n_t
Prior to combustion	1	1	0	2	4
At equilibrium	1-y	1-0.5y	y	2	4-0.5y

- At equilibrium

$$K_P = \frac{n_{SO3}}{n_{SO2} n_{O2}^{1/2}} \left(\frac{P}{n_t}\right)^{-1/2}$$

$$= \frac{y}{(1-y)(1-0.5y)^{1/2}} \left(\frac{2}{4-0.5y}\right)^{-1/2} = 1.8 \quad \rightarrow y = 0.53$$

van't Hoff's equation

$$K_P = A\exp\left(-\frac{B}{T}\right)$$

Example

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \leftrightarrow NO$$

$$K_{P,NO} = 4.71\exp\left(-\frac{10{,}900}{T}\right)$$

Table 3-2. Table of equilibrium constant, **ln** (K_P)

T (K)	$\ln(K_P)$			
	½O_2+½N_2↔NO	CO_2+H_2↔CO+H_2O	CO_2↔CO+ ½O_2	H_2O↔H_2+½ O_2
298	-35.052	-11.554	-103.762	-92.208
500	-20.295	-4.9252	-57.616	-52.691
1000	-9.388	-0.366	-23.529	-23.163
1200	-7.569	0.3108	-17.871	-18.182
1400	-6.27	0.767	-13.842	-14.609
1600	-5.294	1.091	-10.83	-11.921
1800	-4.536	1.328	-8.497	-9.826
2000	-3.931	1.51	-6.635	-8.145
2200	-3.433	1.648	-5.12	-6.768
2400	-3.019	1.759	-3.86	-5.619

Equilibrium Combustion Example 2

A fuel oil contains 87% by mass carbon and 13% by mass hydrogen. Combustion occurs at $\phi = 1$.

Determine the equilibrium concentrations of CO, CO_2, H_2, H_2O, O_2 and N_2 at 2000 K under atmospheric pressure.

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Step 1.
Determine the effective fuel composition, $C_\alpha H_\beta$

Element	Mass fraction	g/100 g fuel	Moles /100 g fuel	Moles /mole C
C	0.87	87	87/12 =7.25	1
H	0.13	13	13/1=13.0	1.793

$CH_{1.793}$

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Step 2.
Stoichiometric chemical reaction formula

- *Stoichiometric reaction with air*

$$CH_{1.793}+1.448\ (O_2+3.76N_2)$$
$$\rightarrow CO_2+0.896H_2O+(1.448x3.76)N_2$$

- *Determine equilibrium composition for stoichiometric combustion with air*

$$CH_{1.793}+1.448\ (O_2 + 3.76N_2)\rightarrow$$

$$(1\text{-}x)CO_2 + xCO + (0.896\text{-}y)H_2O + yH_2$$
$$+(x/2 +y/2)O_2+5.472\ N_2$$

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Step 3:
Identify the equilibrium reactions

The products : CO_2, CO, H_2O, H_2, O_2, ~~N_2~~

$$\begin{cases} CO_2 + H_2 \leftrightarrow CO + H_2O \\ CO_2 \leftrightarrow CO + \frac{1}{2} O_2 \end{cases}$$

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Step 4: Determine equilibrium constants for T_a = 2000 K using Table 3-2

- *Find the equilibrium constants from* Table 3-2 *for*

$$CO_2 \leftrightarrow CO + \frac{1}{2} O_2$$

Table 3-2. Table of equilibrium constant, *ln (K_P)*

T (K)	$CO_2 \leftrightarrow CO + ½O_2$
…	…
1200	-17.871
1400	-13.842
1600	-10.83
1800	-8.497
2000	-6.635
…	…

Approximate value, depending on source

K_2 (2000K) = exp(-6.635)
= 0.00131

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Also find the equilibrium constants from Table 3.2 *for*

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

K_1(2000 K)= exp(1.51) = 4.527

$$CO_2 \leftrightarrow CO + \frac{1}{2} O_2$$

K_2 (2000K) = exp(-6.635) = 0.00131

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Step 5: Determine equilibrium constants using moles of species in the equilibrium mixture

$CH_{1.793}+1.448\ (O_2 + 3.76N_2) \rightarrow$

$(1-x)CO_2 + xCO + (0.896-y)H_2O + yH_2+(x/2 + y/2)O_2+5.472\ N_2$

$n_{CO2}=1-x$ $n_{H2}=y$

$n_{CO}= x$ $n_{O2}=x/2+y/2$

$n_{H2O}=0.896-y$ $n_{N2}=5.472$

$n_{total}=1+0.896+5.472+x/2+y/2 =7.368+x/2+y/2$

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$CH_{1.793}$+1.448 (O_2 + 3.76N_2) →

(1-x)CO_2 + xCO + (0.896-y)H_2O + yH_2+(x/2 +y/2)O_2+5.472 N_2

$$CO_2 \leftrightarrow CO + \tfrac{1}{2}O_2 \qquad K_2 = \frac{n_{CO} \cdot n_{O_2}^{1/2}}{n_{CO_2}}\left(\frac{P_t}{n_{total}}\right)^{1/2}$$

n_{CO2}=1-x n_{O2}=x/2+y/2

n_{CO}= x n_{total}=7.368+x/2+y/2

P_t=1 atm

$$K_2 = \left(\frac{x}{1-x}\right)\left(\frac{x+y}{2}\right)^{1/2}\left(\frac{1}{7.36+\frac{x}{2}+\frac{y}{2}}\right)^{1/2}$$

$$K_2 = \left(\frac{x}{1-x}\right)\left(\frac{x+y}{14.72+x+y}\right)^{1/2}$$

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Similarly (actually simpler, because (c+d)-(a+f)=0)

$$\mathrm{CO_2 + H_2 \leftrightarrow CO + H_2O} \qquad CO_2 \leftrightarrow CO + \tfrac{1}{2}O_2$$

$$K_1 = \left(\frac{x}{1-x}\right)\left(\frac{0.896-y}{y}\right) \qquad K_2 = \left(\frac{x}{1-x}\right)\left(\frac{x+y}{14.72+x+y}\right)^{1/2}$$

K_1(2000 K)= 4.527 K_2 (2000K) = 0.00131

$$\begin{cases} \left(\frac{x}{1-x}\right)\left(\frac{0.896-y}{y}\right) = 4.527 \\ \left(\frac{x}{1-x}\right)\left(\frac{x+y}{14.72+x+y}\right)^{1/2} = 0.00131 \end{cases}$$

How to solve these equations?

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With x=0.027, y=0.0055

$$CH_{1.793}+1.448\ (O_2 + 3.76N_2) \rightarrow$$

$$(1-x)CO_2 + xCO + (0.896-y)H_2O + yH_2+(x/2 + y/2)O_2+5.472\ N_2$$

$$CH_{1.793}+1.448\ (O_2 + 3.76N_2) \rightarrow$$

$$0.973CO_2 + 0.027CO + 0.8905H_2O + 0.0055H_2+0.01625O_2+5.472\ N_2$$

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Discussion

- Stoichiometric reaction without equilibrium

$$CH_{1.793}+1.448\ O_2 \rightarrow$$

$$CO_2+0.896H_2O+5.472N_2$$

- Stoichiometric reaction with equilibrium

$$CH_{1.793}+1.448\ (O_2 + 3.76N_2) \rightarrow$$

$$0.973CO_2 + 0.8905H_2O + 0.027CO + 0.0055H_2+0.01625O_2 +5.472\ N_2$$

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Combustion Temperature

from Review of Thermodynamics

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Heat added to system, Q

- Consider a constant pressure combustion

$$Q = \sum_P n_i h_i(T_p) - \sum_R n_i h_i(T_R)$$

- ❑ n = molar fraction of the component in fuel-air mixture or the product
- ❑ $h(T)$ = enthalpy of a component at temperature T in J/mole.
- ❑ Subscript i, P and R stand for the ith component, product, and reactant, respectively.

- Note that the temperature of the reactants may not be the same as that of the products.
- Therefore, the calculated heat production is temperature dependent.
- When they are the same, it becomes the enthalpy of reaction.

Enthalpy of Reaction, ΔH_R

- Q (Tp=TR) $\Delta H_R = \sum_P n_i h_i(T_p) - \sum_R n_i h_i(T_R)$ in J/mole of fuel

$$= \sum_P n_i h_i(T_o) - \sum_R n_i h_i(T_o)$$

Heat of Combustion / Heating Value

- The maximum heat added to a combustion system is called the **heat of combustion** or the **heating value**.
- The maximum amount of heat is released when the combustion is **stoichiometric**
- Heat is not wasted to heat either fuel or air composition

Higher/Lower heating value

- HHV is used when the water in the products is in the liquid state ($h_{H20} = h_l$).
- LHV is used when the water in the products is in the vapor state ($h_{H2o} = h_g$),
- the energy required to vaporize the water is not considered in the heat of combustion.

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Table A-5. Higher and Lower Heating Values of Typical Fuels

Fuel	Mass based (MJ/kg)	Molar based (kJ/mole)
Coal	15–27	200–350
Diesel	44.8	-
Gasoline	47.3	-
Ethane	51.9	1570
Hydrogen	141.8	286
Methane	55.5	783
Propane	50.35	2220
Butane	49.5	2875
Paraffin	46	16,300
Wood	15	300
Peat	6–15	-

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Enthalpy of formation, h_f^o

- The change of enthalpy that accompanies the formation of 1 mole of compound in its standard state from its constituent elements in their standard states.
- The standard state: P_0=101.325 kPa; T_0=298 K
- Values for standard heat of formation for different species are tabulated in Table A-4.

Species	Δh_f^o (298 K) (J/mole)
C(s)	0
CH	594,983
CH_2	385,775
CH_3	145,896
CH_4	-74,980

The enthalpy of formation of every element in its natural state at the standard conditions is zero.

Table A-4. Approximate thermodynamic data for species of combustion interest

Enthalpy of formation (cont…)

- Could be positive or negative
  - o Negative = Releases heat in formation
  - o Positive = Takes energy to form

$$\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)$$

$$h^o_{f,\,H_2O} = \text{-286,000 kJ/kmol}$$

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$h^o_{f,\,CO_2} = \text{-394,000 kJ/kmol}$$

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Enthalpy Scale for A Combustion System

- In general heat release from reactants to products

$$Q = \sum_P n_i h_i(T_p) - \sum_R n_i h_i(T_R)$$

$$h(P,T) = h(STP) + [h(P,T) - h(STP)] = h^o_{f,i} + [h_i(P,T) - h_i(STP)]$$

$$\Rightarrow \quad h_i(T) = h^o_{f,i} + \int_{298K}^{T} C_{p,i}\, dT$$

$C_{p,i}(T) = a_i + b_i T$ (Table A-4)

$$\Rightarrow \quad h_i(T) = h^o_{f,i} + a_i(T - T_{298K}) + \frac{1}{2} b_i (T^2 - T_{298K}{}^2)$$

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Table A-4. Approximate thermodynamic data for species of combustion interest

Species	Δh^o_f (298 K) (J/mol)	C_p=a+bT (J/mol.K)	
		a	b
C	716,033	20.5994	0.00026
C(s)	0	14.926	0.00437
CH	594,983	27.6451	0.00521
CH_2	385,775	35.5238	0.01000
CH_3	145,896	42.8955	0.01388
CH_4	-74,980	44.2539	0.02273

$$\Longrightarrow \quad h_i(T) = h^o_{f,i} + a_i(T - T_{298K}) + \frac{1}{2} b_i (T^2 - T_{298K}{}^2)$$

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Steps for calculating heat generation

1. Fuel formula, equivalent ratio, mixture temperature
2. Chemical reaction formula (Combustion stoichiometry)
3. Table A-4 for $h^o_{f,i}$, $\mathrm{a_i}$, $\mathrm{b_i}$

$$h_i(T) = h^o_{f,i} + \mathrm{a_i}(\mathrm{T} - \mathrm{T_{298K}}) + \frac{1}{2}\mathrm{b_i}(\mathrm{T}^2 - \mathrm{T_{298K}}^2)$$

$$Q = \sum_P n_i h_i(T_p) - \sum_R n_i h_i(T_R)$$

Two unknowns (Q and Tp) in one equation

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Adiabatic Flame Temperature (Q=0)

- The **constant volume adiabatic flame temperature** is the temperature of the products as a result of a complete combustion process that takes place without any work done to the surroundings as the volume of the combustion system remains constant.
- The **constant pressure adiabatic flame temperature** is the temperature of the products resulting from a complete combustion process that occurs without heat transfer to the surroundings; however work is done on the surroundings.
- the constant pressure flame temperature is lower than that of a constant volume process because some of the energy is utilized to change the volume of the system.
- for either one of the definitions, the combustion system is adiabatic (i.e. $Q = 0$).

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Constant Pressure Adiabatic Flame Temperature

$$Q = \sum_P n_i h_i(T_a) - \sum_R n_i h_i(T_R) = 0$$

- T_a =Adiabatic temperature; T_R =Reactant temperature

$$\sum_R n_i \left[h^o_{f,i} + \left(h_i(T_R) - h_i(298K)\right)\right] = \sum_P n_i \left[h^o_{f,i} + \left(h_i(T_a) - h_i(298K)\right)\right]$$

$$h_i(T_R) = \left(a_i(T_R - 298K) + \frac{b_i}{2}(T_R{}^2 - (298K)^2 \right)$$

$$h_i(T_a) = \left(a_i(T_a - 298K) + \frac{b_i}{2}(T_a{}^2 - (298K)^2 \right)$$

$$\sum_R n_i \left[\left(a_i(T_R - 298K) + \frac{b_i}{2}(T_R{}^2 - (298K)^2 \right) + h^o_{f,i} \right]$$

$$= \sum_P n_i \left[\left(a_i(T_a - 298K) + \frac{b_i}{2}(T_a{}^2 - (298K)^2 \right) + h^o_{f,i} \right]$$

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If T_R = T_0 =298 K

- As a common simplification, the temperature of the air-fuel mixture before combustion is assumed to be of standard temperature, T_R =298 K =T_0. In this case, the formula above is simplified as,

$$\sum_R n_i h^o_{f,i} = \sum_P n_i \left[\left(a_i(T_a - 298K) + \frac{b_i}{2}(T_a{}^2 - (298K)^2 \right) + h^o_{f,i} \right]$$

This equation could be solved now!

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Example

- CH_4 is burned in air at 298 K at an equivalence ratio of 1.0 and the combustion is complete. Determine the constant pressure adiabatic flame temperature.

Solution

Step 1. *Set up stoichiometric combustion reaction equation*

$$CH_4+2(O_2+3.76N_2) \rightarrow CO_2 + 2H_2O+7.52N_2$$

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$CH_4+2(O_2+3.76N_2) \leftrightarrow CO_2 + 2H_2O+7.52N_2$

Step 2

- *For an adiabatic constant pressure system, Q=0, W =0, first law of thermodynamics gives*

$$\sum_R n_i \left[\left(a_i (T_R - 298K) + \frac{b_i}{2}(T_R^{\,2} - (298K)^2 \right) + h^o_{f,i} \right]$$

$$= \sum_P n_i \left[\left(a_i (T_a - 298K) + \frac{b_i}{2}(T_a^{\,2} - (298K)^2 \right) + h^o_{f,i} \right]$$

- *Since $T_R = T_0$ =298 K, left hand side (LHS) of this equation is simplified as*

$$LHS = \sum_R n_i h^o_{f,i} = h^o_{f,CH_4} + 2h^o_{f,O_2} + 7.52h^o_{f,N_2}$$

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The right hand side (RHS) of the equation is

$$RHS = \left[\left(a_{CO_2}(T_a - 298K) + \frac{b_{CO_2}}{2}(T_a{}^2 - (298K)^2\right) + h^o_{f,CO_2}\right]$$

$$+2\left[\left(a_{H_2O}(T_a - 298K) + \frac{b_{H_2O}}{2}(T_a{}^2 - (298K)^2\right) + h^o_{f,H_2O}\right]$$

$$+7.52\left[\left(a_{N_2}(T_a - 298K) + \frac{b_{N_2}}{2}(T_a{}^2 - (298K)^2\right) + h^o_{f,N_2}\right]$$

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$CH_4+2(O_2+3.76N_2) \rightarrow CO_2 + 2H_2O+7.52N_2$

Step 3: $h^o_{f,i}$ a_i, b_i

Species	$h^o_{f,i}$ [J/mole]	$C_p(T)$ [J/mole. K]	
		a_i	b_i
CO_2	-394,088	44.3191	0.0073
H_2O	-242,174	32.4766	0.00862
N_2	0	29.2313	0.00307
O_2	0	30.5041	0.00349
CH_4	-74,980	44.2539	0.02273

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$$LHS = [-74{,}980] + 2[0] + 2(3.76)[0] = -74{,}980\ (J/mol)$$

$$RHS = \left[\left(44.3191(T_a - 298) + \frac{0.0073}{2}(T_a{}^2 - (298K)^2\right) - 394{,}088\right]$$

$$+ 2\left[\left(32.4766(T_a - 298K) + \frac{0.00862}{2}(T_a{}^2 - (298K)^2\right) - 242{,},174\right]$$

$$+ 2(3.76)\left[\left(29.2313(T_a - 298K) + \frac{0.00307}{2}(T_a{}^2 - (298K)^2\right) + 0\right]$$

→ $0.02387\ T_a{}^2 + 330.26\ T_a - 903994 = 0$

→ $T_a = 2341\ (K)$

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Adiabatic Flame Temperature for Products at Equilibrium

Fuel oil contains 87% by mass carbon and 13% by mass hydrogen. Specific gravity of the fuel oil is 825 kg/m^3. The higher heating value (HHV) = 3.82×10^{10} J/m^{3}and combustion occurs at ϕ=1. Initial temperature of the fuel oil and combustion air is 25 ^{o}C = 298 K.

- *Determine the adiabatic flame temperature and equilibrium concentrations of CO, CO_2, H_2, H_2O, O_2 and N_2.*

- *See textbook for solution*

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Summary of Chapter 3

- Basic chemical properties of gases
- Combustion basics
- Stoichiometry
- Chemical equilibrium and chemical kinetics
- Adiabatic temperature

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