Chemical Reactions

When analyzing reacting systems, we need to consider the chemical internal energy, which is the energy associated with the destruction and formation of chemical bonds between the atoms. Thermodynamic analysis of reactive mixtures is primarily an extension of the principles we have learned thus far; however, it is necessary to modify the methods used to calculate specific enthalpy, internal energy and entropy.

Definitions

Fuel: any material that can be burned to release thermal energy. Most familiar fuels are hydrocarbons and are denoted by the general formula of C_nH_m. For example octane is C_8H_{18}.

Combustion: is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released. The oxidizer is often air.

Reactants: are the components that exist before the reaction.

Products: are the components that exist after the reaction.

Ignition temperature: the minimum temperature at which a fuel starts to burn.

Dry air is composed of 20.9% O_2, 78.1% N_2, 0.9% Ar, and small amounts of CO_2, He, Ne, H_2. In combustion analyses, Ar is treated as N_2, and other gases are neglected. Then dry air can be approximated as 21% O_2 and 79% N_2 by mole numbers.

$$1 \; kmol \; O_2 + 3.76 \; kmol \; N_2 = 4.76 \; kmol \; air$$
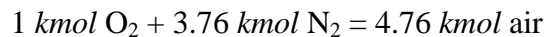
(0.79/0.21 = 3.76) Note: from the Amagat model, we know that a mixture at a known T and P (as is the case with combustion reactions):

$$\frac{n_i}{n} = \frac{V_i}{V}$$

Therefore, by expressing a mixture in terms of the number of moles we are also expressing it in terms of a volume fraction.

During combustion, nitrogen behaves as an inert gas and does not react with other elements. However; N_2 greatly affects the outcome of a combustion process, since it enters in large quantities and at low temperature, absorbing portion of the chemical energy released during combustion.

In most combustion processes, the moisture in air and the H_2O that forms during combustion can be treated as an inert gas, like nitrogen. It is important to predict the *dew-point* temperature of the water vapor since the water droplets often combine with the sulfur dioxide (that may be present) forming sulfuric acid which is highly corrosive.

Air Fuel Ratio

It is expressed on a mass basis and defined as:

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{N_{air}\left(M_{air}\right)}{N_{fuel}\left(M_{fuel}\right)} \qquad M_{air} = 28.97 \cong 29 \; kg \, / \, kmol$$

Where N is the number of moles and M is the molar mass.

Theoretical (Stoichiometric) Air

The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air.

A combustion process is complete if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2. That is, all the combustible components of a fuel are burned to completion during a complete combustion process.

The ideal combustion process during which a fuel is burned completely with stoichiometric air is called theoretical (or stoichiometric) combustion. For example, the theoretical combustion of methane is:
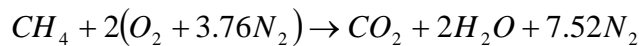
$$CH_4 + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2$$
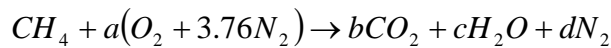
where

$C:\qquad b = 1$

$H:\qquad 2c = 4$

$O:\qquad 2b + c = 2a$

$N:\qquad d = 3.76a$

Solving these equations, the <u>balanced chemical</u> reaction is:

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

The amount of combustion air is 2 moles of oxygen plus 2 x 3.76 moles of nitrogen, giving a total of 9.52 moles of air per mole of fuel. The air fuel (AF) ratio for the above combustion on a mass basis is:

$$AF = \frac{9.52 \times 28.97}{1 \times 16.04} = 17.19 \; kg \; air / kg \; fuel$$

That means 17.19 kg of air is used to burn each kilogram of methane.

In actual combustion processes, it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion or to control the temperature of the combustion chamber. The amount of air in excess of the stoichiometric amount is called excess air.

The amount of excess air is usually expressed in terms of the stoichiometric air as percent excess air or percent theoretical air. For example 150% = 1.5 × the theoretical air.

Also, it may be referred to as 20% excess air; i.e., 120% stoichiometric air.

The amount of air used in combustion processes is also expressed in terms of the equivalent ratio:

$$Equivalent \; ratio = \frac{AF_{actual}}{AF_{theoretical}} \begin{cases} >1 & \text{lean mixture (excess air)} \\ <1 & \text{rich mixture (not enough air)} \end{cases}$$

Amounts of air less than the stoichiometric amount are called deficiency of air and often expressed as percent deficiency of air.

Enthalpy of Formation

During a chemical reaction, some chemical bonds that bind the atoms into molecules are broken, and new ones are formed. Thus a process that involves chemical reactions involves changes in chemical energies, which must be accounted for in an energy balance.

It is necessary to choose a common base as the reference state and assign a value of zero to the internal energy or enthalpy of a substance at that state. The chosen reference is known as *standard reference state*:

25˚C and 1 atm.

Property values at the standard reference state are indicated by a superscript (˚), e.g. $h°$ and $u°$.

Enthalpy of reaction, h_R: 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.

Enthalpy of combustion, h_C: 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

$$h_R = h_C = H_{products} - H_{reactants}$$

Enthalpy of formation, $\overline{h}_f$: the enthalpy of a substance at a specified state due to its chemical composition.

We assign the enthalpy of formation all stable elements (such as O_2, N_2, H_2) a value of zero at the standard reference state of 25˚C and 1 atm.

Consider the formation (burning) of CO_2 from its elements at 1 atm during a steady-flow process:

$$C + O_2 \rightarrow CO_2$$
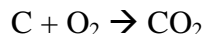
The enthalpy change during this process was determined to be – 393,520 kJ/kmol. However; $H_{react} = 0$. Thus the enthalpy of formation of CO_2 at standard reference state is:

$$\overline{h}_{f,CO_2}° = -393,520 \text{ kJ/kmol}$$

The negative sign is due to the fact that chemical energy is released (exothermic process) during the formation of CO_2. The positive value indicates heat is absorbed (endothermic process). See Table A-26 for the enthalpy of formation of chemical substances.

Heating Value: is defined as 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. That is the absolute value of the enthalpy of combustion of fuel.

Higher Heating Value (HHV): when the water in the products is in the liquid form.

Lower Heating Value (LHV): when the water in the products is in the vapor form.

$$HHV = LHV + \left(mh_{fg}\right)_{H_2O} \quad \left(kJ / kg \; fuel\right)$$

HHV and LHV of common fuels are given in Table A-27.

First-Law Analysis of Reacting Systems

1) Steady-flow System

We express the enthalpy in such a form that is relative to the standard reference state and the chemical energy term appears explicitly. Thus it reduces to the enthalpy of formation at the standard reference state plus sensible enthalpy relative to a reference state, i.e., 25°C and 1 atm:

$$Enthalpy = \bar{h}_f^{\circ} + \left(\bar{h} - \bar{h}^{\circ}\right) \quad \left(kJ / kmol\right)$$

Where the term in the parentheses represents the sensible enthalpy relative to the standard reference state.
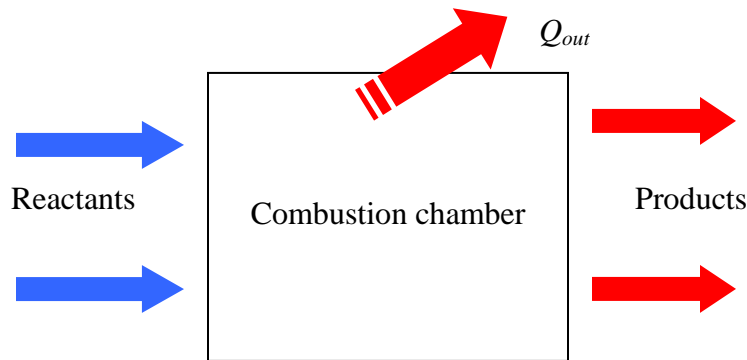

Fig.1: The first-law for reacting mixtures.

The first-law for a chemically reacting steady-flow system can be expressed as:

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

Where $\dot{n}_p$ and $\dot{n}_r$ represent the molal flow rates of the products p and the reactants r, respectively. Or on a mole of fuel basis:

$$Q_{in} + W_{in} + \sum N_r \left(\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ}\right)_r = Q_{out} + W_{out} + \sum N_p \left(\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ}\right)_p$$

Where N_r and N_p represent the number of moles of the reactants r and the product p, respectively. The first-law can also be written as:

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

Where

$$H_{prod} = \sum N_p \left(\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ}\right)_p \quad \left(kJ / kmol \; fuel\right)$$

$$H_{react} = \sum N_r \left(\bar{h}_f^{\circ} + \bar{h} - \bar{h}^{\circ}\right)_r \quad \left(kJ / kmol \; fuel\right)$$

Remember that the heat transfer to the system and work done by the system are considered positive quantities.

2) Closed System

The energy balance for a chemically reacting closed system can be expressed as:

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

where U represents the internal energy. To avoid using another property – the internal energy of formation- we use the definition of enthalpy $u = h - Pv$. Thus, the first-law becomes for closed systems:

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

Term $P\bar{v}$ is negligible for solids and liquids, and can be replaced by $R_u T$ assuming ideal gas.

Example

Liquid propane (C_3H_8) enters a combustion chamber at 25˚C at a rate of 0.05 kg/min where it mixed and burned with 50% excess air that enters the combustion chamber at 7˚C. An analysis of combustion chamber reveals that all the hydrogen in the fuel burns to H_2O but only 90% of the carbon burns to CO_2 with the remaining 10% forming CO. If the exit temperature of the combustion gases is 1500 K, determine
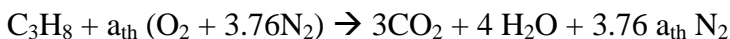
    a) The mass flow rate of air

    b) The rate of heat transfer from the combustion chamber.

Assumptions:

- Steady operating condition
- Air and the combustion gases are ideal gases
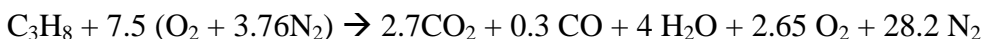- Kinetic and potential energies are negligible.

Analysis:

The theoretical amount of air is determined from the stoichiometric reaction:

$C_3H_8 + a_{th} (O_2 + 3.76N_2) \rightarrow 3CO_2 + 4 H_2O + 3.76 a_{th} N_2$

O_2 balance gives $\rightarrow a_{th} = 3 + 2 = 5$

Then the balanced equation for the actual combustion process with 50% excess air and some CO becomes (5 x 1.5 = 7.5):

$C_3H_8 + 7.5 (O_2 + 3.76N_2) \rightarrow 2.7CO_2 + 0.3 CO + 4 H_2O + 2.65 O_2 + 28.2 N_2$

a) the air-fuel ratio for this combustion process is:

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{7.5 \times 4.76 kmol(29 kg / kmol)}{3 kmol(12 kg / kmol) + 4 kmol(2 kg / kmol)} = 25.53 \ kg \ air / kg \ fuel$$

thus;

$$\dot{m}_{air} = AF(\dot{m}_{fuel}) = 1.18 \ kg \ air / \min$$

b) The heat transfer for this steady-flow combustion process is determined from an energy balance per unit mole of fuel:

$$Q_{out} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p$$

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$.

Substance	$\bar{h}_f^\circ$ kJ/kmol (Table A-26)	$\bar{h}_{280K}$ kJ/kmol (Table A-18,19)	$\bar{h}_{298K}$ kJ/kmol	$\bar{h}_{1500K}$ kJ/kmol
C_3H_8 (l)	-118,910	-	-	-
O_2	0	8150	8682	49,292
N_2	0	8141	8669	47,073
H_2O (g)	-241,820	-	9904	57,999
CO_2	-393,520	-	9364	71,078
CO	-110,530	-	8669	47,517

Note that:

$$\bar{h}_f^\circ \big|_{C_3H_8}(l) = \bar{h}_f^\circ \big|_{C_3H_8}(g) - \bar{h}_{fg}$$

Q_{out} = (1 kmol C_3H_8)[(-118,910 + h_{298} – h_{298}) kJ/kmol C_3H_8]

+ (7.5 kmol O_2)[(0 + 8150 – 8682) kJ/kmol O_2]

+ (28.2 kmol N_2) [(0 + 8141 – 8669) kJ/kmol N_2]

– (2.7 kmol CO_2) [(-393,520 + 71078 – 9364) kJ/kmol CO_2]

– (0.3 kmol CO) [(-110,530 + 47,517 – 8669) kJ/kmol CO]

– (4 kmol H_2O)[(-241,820 + 57,999 – 9904) kJ/kmol H_2O]

– (2.65 kmol O_2)[(0 + 49,292 – 8682) kJ/kmol O_2]

– (28.2 kmol N_2)[(0 + 47,073 – 8669) kJ/kmol N_2]

= 363,880 kJ/kmol of C_3H_8 = 363,880/44 = 8270 kJ/kg of C_3H_8

Then the rate of heat transfer for a mass flow rate of 0.05 kg/min for propane becomes:

$$\dot{Q}_{out} = \dot{m}q_{out} = (0.05 kg / \min)(8270 kJ / kg) = 413.5 \ kJ / \min = 6.89 \ \text{kW}$$

Adiabatic Flame Temperature

When the combustion chamber is insulated (no heat loss to the surroundings), the temperature of the products reaches a maximum which is called the *adiabatic flame* or *adiabatic combustion temperature* of the reaction.

In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical consideration. Therefore, the adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles. The max temperature can be controlled by adjusting the amount of excess air which serves as coolant.
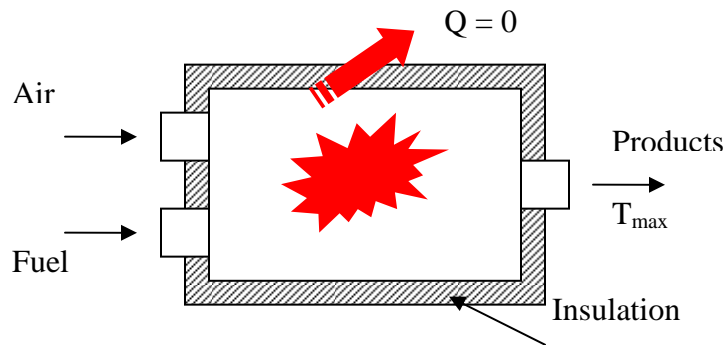
The adiabatic flame temperature of a steady-flow combustion process is determined from an energy balance when $Q = 0$:

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

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

The determination of the adiabatic flame temperature requires the use of an iterative technique such as the one described below:

An adiabatic temperature (T_{adi}) is guessed.

Step 1: Calculate the H_{react} based on known values of T_{react} and T_{ref}.

Step 2: Calculate the H_{prod} based on the guessed value of T_{adi} and T_{ref}.

Step 3: Repeat Step 2, until $H_{react} = H_{prod}$.

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

3) The amount of air used.

Note that the adiabatic flame temperature attains its maximum value when complete combustion occurs with the theoretical amount of air (0% excess air).

Entropy Change of Reacting Systems

The entropy balance for any system undergoes any process can be expressed as:

$$\underbrace{S_{in} - S_{out}}_{\substack{\text{Net entropy transfer by} \\ \text{heat and mass}}} + S_{gen} = \Delta S_{system}$$

Using quantities per unit mole of fuel and taking positive direction of heat transfer to the system; entropy balance becomes:

$$\sum \frac{Q_k}{T_k} + S_{gen} = S_{prod} - S_{react} \qquad (kJ / K)$$

For an adiabatic process, we obtain:

$$S_{gen} = S_{prod} - S_{react} \quad \geq 0$$

It should be noted that for the entropy balance for a reacting system involves calculating the entropies for components (reactants and products) not the entropy changes. Thus, we need a common base for the entropy of all substances, as we did with enthalpy.

The third law of thermodynamics provides an absolute base for the entropy values for all substances. According to the third law of thermodynamics, *the entropy of a pure crystalline substance at absolute zero temperature is zero.*

- the entropy relative to this datum (0 K) is called absolute entropy

- absolute entropy at 1 atm and temperature T is denoted as $s^\circ(T), \bar{s}^\circ(T)$ for a per unit mass or per mole basis

- while h was only a function of temperature for ideal gases, we must account for the effects of both T and P in entropy:

$$\bar{s}(T,P) = \bar{s}^\circ(T,P_0) - R_u \ln \frac{P}{P_0}$$

Where Ru = 8.314 *kJ/kmol.K* is the universal gas constant.

Note that temperature of a component is the same as the temperature of the mixture and the partial pressure of a component is equal to the mixture pressure multiplied by the mole fraction of the component:

For the component "i" $\begin{cases} T_i = T_{mixture} \\ P_i = y_i P_{mixture} \end{cases}$

For the component i of an ideal-gas mixture, this relationship can be written as:

$$\bar{s}_i(T,P_i) = \bar{s}_i^\circ(T,P_0) - R_u \ln \frac{y_i P_m}{P_0} \qquad (kJ / kmol \cdot K)$$

Where $P_0 = 1$ atm, P_i is the partial pressure, y_i is the mole fraction of the component, and P_m is the total pressure of the mixture.