

Importance of Combustion

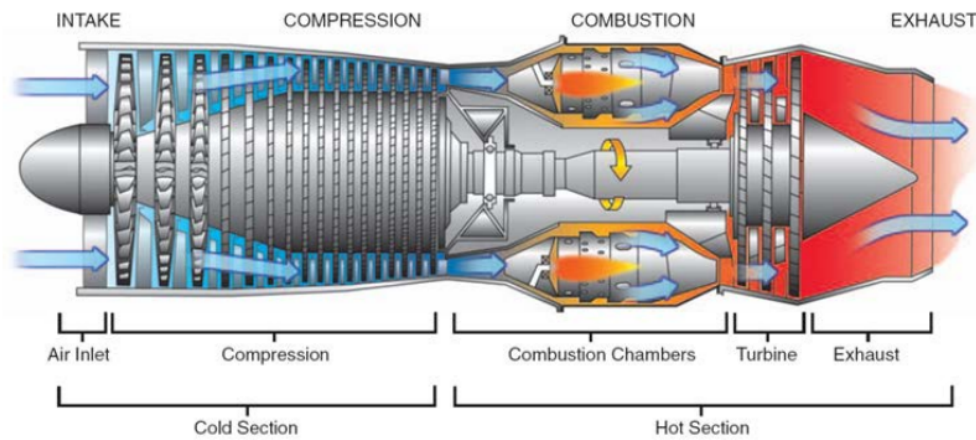


Figure 1:

Combustion is predominant source of useful energy, and predominant source of pollutant and CO₂ emissions.

What Is Combustion?

Chemical Reaction:

- Bonds within the molecules of the reactants are broken.
- Atoms and electrons are rearranged to **form new chemical species** called products.

Combustion:

- Rapid oxidation of fuel for heat release:



0.1 Global and Elementary Reactions

0.1.1 Study of Chemical Reactions

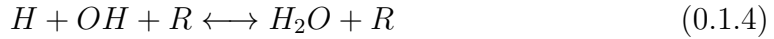
Overall/Global Reaction

Statement of mass and number of atoms conservation.



Elementary Reaction

Direct results of collisions between reactant molecules. Combustion usually consists of a large set of elementary reactions, e.g. hydrogen combustion:



Chemical Kinetics: Study of mechanisms and rates of chemical change.

0.1.2 Chemical Complexity

Reality: Detailed chemical mechanisms involve a huge number of elementary reactions and intermediate species.

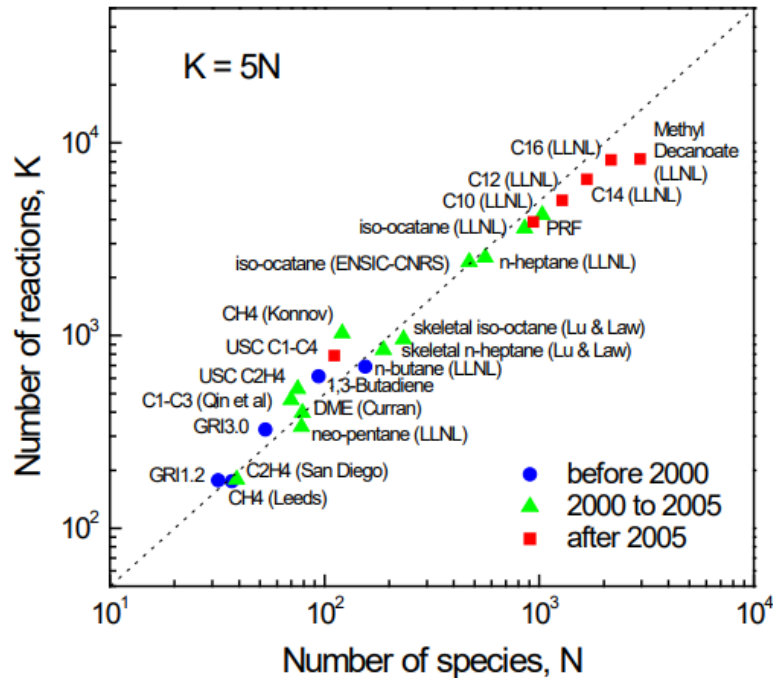


Figure 2:

0.1.3 Fuel and Oxidizer

Fuel:

- Liquids: e.g. gasoline, diesel, kerosene;
- Gases: e.g. natural gas;
- Solids: e.g. coal.
- Most common fuels : **Hydrocarbons** (C_xH_y), e.g., Methane (CH_4), propane (C_3H_8), octane (C_8H_{18}), gasoline (average $C_{7.2}H_{12.6}$), diesel (average $C_{12}H_{23}$)
- Bio-fuels : **Usually** ($C_xH_yO_z$), e.g., Methanol (CH_3OH), ethanol (C_2H_5OH)

Oxidizer:

- In most combustion applications, air provides the needed oxygen;
- However, pure oxygen (O_2) can be used, called oxy-fuel combustion, for carbon capture and storage

0.1.4 Fuel Composition

Fuel	Hydrogen/Carbon Ratio	Formula
Hydrocarbons	y/x	C_xH_y
Gasoline/Petrol	1.87	$C_xH_{1.87x}$
Diesel	1.7 ~ 1.8	$C_xH_{1.7-1.8x}$
Natural Gas (Methane)	4	CH_4
Coal	0.8	$C_xH_{0.8x}$
Hydrogen	∞	H_2
Alcohol (Methanol)	4	CH_4O

Figure 3:

0.2 Combustion in Air

Combustion in Dry Air:

Fuel (F)+Dry Air (A) \longrightarrow Carbon Dioxide (CO_2) + Water (H_2O) + Nitrogen (N_2)
 Dry Air (A) = 21% by volume of Oxygen (O_2) + 79% by volume of Nitrogen (N_2)
 = 1 unit volume of Oxygen (O_2) + 3.76 unit volume of Nitrogen (N_2)

Combustion in Moist Air:

Fuel (F) + Moist Air (A) \longrightarrow Carbon Dioxide (CO_2) + Water (H_2O) + Nitrogen (N_2)
 Moist Air (A) = 1 unit mass of Oxygen (O_2) + 3.29 unit mass of Nitrogen (N_2)
 +4.29 ω unit mass of Water Vapour (H_2O)

0.2.1 Air/Fuel Ratio and Fuel/Air Ratio

Air/Fuel Ratio by Mass:

$$AF = \frac{\text{mass of air } (m_{air})}{\text{mass of fuel } (m_{fuel})} = \frac{x_{air}}{x_{fuel}} = \frac{n_{air}}{n_{fuel}} \frac{M_{air}}{M_{fuel}} \quad (0.2.1)$$

Fuel/Air Ratio by Mass:

$$FA = \frac{1}{AF} \quad (0.2.2)$$

Air/Fuel Ratio by Volume:

$$\overline{AF} = \frac{\text{volume of air } (V_{air})}{\text{volume of fuel } (V_{fuel})} = \frac{n_{air}}{n_{fuel}} = \frac{y_{air}}{y_{fuel}} \quad (0.2.3)$$

Relationship:

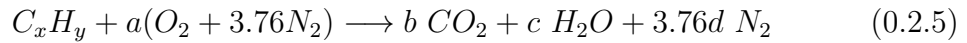
$$AF = \overline{AF} \frac{M_{air}}{M_{fuel}} \quad (0.2.4)$$

0.2.2 Stoichiometric Combustion in Air

Stoichiometry:

Chemically exact proportion of fuel and air for complete burning of fuel.

Stoichiometric Combustion of Hydrocarbons in Dry Air:



Balance of atom number for each element:

$$C : \quad x = b \quad (0.2.6)$$

$$H : \quad y = 2c \quad (0.2.7)$$

$$O : \quad 2a = 2b + c \quad (0.2.8)$$

$$N : \quad 2 \cdot 3.76a = 2 \cdot 3.76d \quad (0.2.9)$$

Therefore, the stoichiometric coefficients:

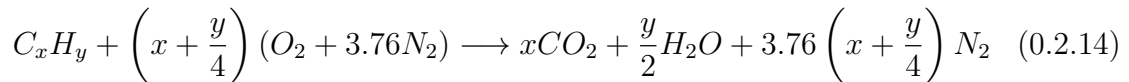
$$b = x \quad (0.2.10)$$

$$c = \frac{y}{2} \quad (0.2.11)$$

$$a = x + \frac{y}{4} \quad (0.2.12)$$

$$d = a \quad (0.2.13)$$

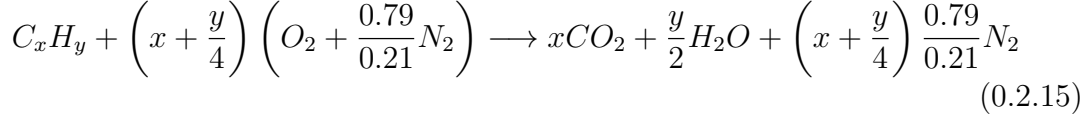
The mass balance equation for stoichiometric combustion:



Note:

- The mass, atom/mole number of each element are conserved.
- The total mass of reactants equals that of the products.
- The total mole numbers of reactants and products are not usually the same.

Stoichiometric Combustion of Hydrocarbons in Air:



Stoichiometric Air/Fuel Ratio (by volume):

$$\overline{AF}_{stoi} = \left(x + \frac{y}{4}\right) \left(1 + \frac{0.79}{0.21}\right) \quad (0.2.16)$$

Stoichiometric Air/Fuel Ratio (by mass):

$$AF_{stoi} = \frac{\left(x + \frac{y}{4}\right) \left(32 + \frac{0.79}{0.21} \cdot 28\right)}{12x + y} \quad (0.2.17)$$

For typical petroleum-based fuels, $AF_{stoi} = 14 \sim 15$.

0.2.3 Equivalence Ratio

Equivalence ratio is a measure of the proportion of fuel and air in a reactive mixture relative to its stoichiometric value.

Equivalence Ratio (by Mass):

$$\phi = \frac{(FA)_{actual}}{(FA)_{stoi}} = \frac{(AF)_{stoi}}{(AF)_{actual}} \quad (0.2.18)$$

Equivalence Ratio (by Volume):

$$\bar{\phi} = \frac{(\overline{FA})_{actual}}{(\overline{FA})_{stoi}} = \frac{(\overline{AF})_{stoi}}{(\overline{AF})_{actual}} \quad (0.2.19)$$

$\phi > 1.0 \longrightarrow$ fuel-rich mixture/combustion

$\phi = 1.0 \longrightarrow$ stoichiometric mixture/combustion

$\phi < 1.0 \longrightarrow$ fuel-lean mixture/combustion

0.2.4 Actual Combustion Process

In an actual process:

- Combustion take places in **tens or hundreds of elementary reactions**.
- Usually a **huge number of intermediate species** are generated.
- A combustion process is almost always **incomplete**.
- In addition to the usual products CO_2 and H_2O , there are **harmful emissions** from combustion such as unburned HC , CO , NO_x and soot.
- The combustion process is strongly affected by fluid dynamics (in particular, **turbulence**) and **mixing**.

0.3 Open System Energy Analysis of Combustion Processes

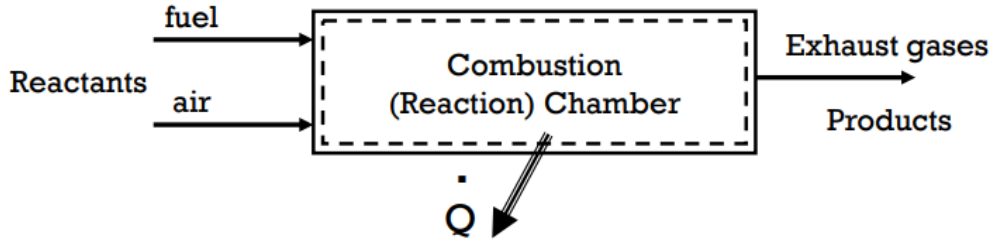


Figure 4:

Assumptions:

- SSSF (steady state simple fluid)
- $\Delta KE = \Delta PE = 0$
- No mechanical work

Steady State Energy Balance:

$$\frac{dE_{CV}}{dt} = \dot{Q} + \dot{W} + \sum_{in} \dot{m}_{in} \left(h + \frac{v^2}{2} + gz \right) - \sum_{out} \dot{m}_{out} \left(h + \frac{v^2}{2} + gz \right) \quad (0.3.1)$$

$$\dot{Q} = \sum_{out} \dot{m}_{out} h_{out} - \sum_{in} \dot{m}_{in} h_{in} \quad (0.3.2)$$

Combustion heat release (on a mass basis):

$$Q = \sum_P (m_i h_i) - \sum_R (m_i h_i) = H_P - H_R \quad (0.3.3)$$

Combustion heat release (on a molar basis):

$$Q = \sum_P (n_i \bar{h}_i) - \sum_R (n_i \bar{h}_i) = H_P - H_R \quad (0.3.4)$$

0.3.1 Energy Change in a Chemical Reaction

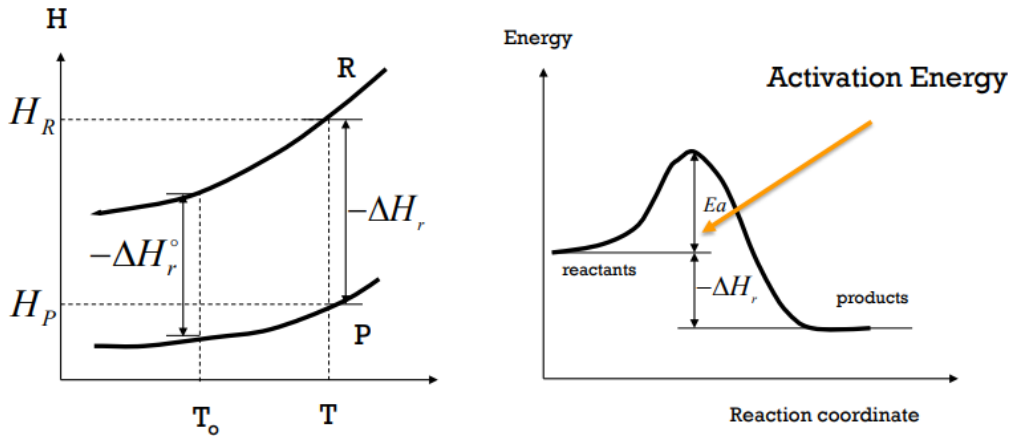


Figure 5:

ΔH_r° is enthalpy change in combustion at standard reference temperature T_o .
 ΔH_r is enthalpy change in combustion at an arbitrary temperature T .

0.4 Enthalpy of Formation

The Enthalpy of Formation of a chemical compound is the enthalpy change associated with the reaction of forming one mole of the compound from its elements in their standard states (gas or solid) at the standard reference conditions:

$$\bar{h}_{f,i}^\circ = \Delta \bar{h}_{f,i}^\circ = \Delta \bar{h}_i (298.15K; 1 \text{ atm}) \quad (0.4.1)$$

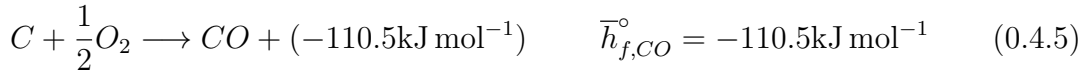
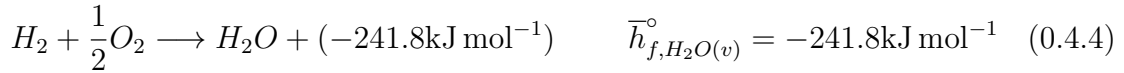
- In exothermic (or endothermic) reaction, the energy is released (or absorbed) when the compound is formed from its elements, so the enthalpy of formation is negative (or positive).
- By definition, the enthalpy of formation for any element (such as H_2 , O_2) at its standard state is zero.

Thus, the enthalpy of any compound i at an arbitrary state becomes:

$$\bar{h}_i(T, p) = \bar{h}_{f,i}^\circ + \left[\bar{h}_i(T, p) - \bar{h}_i(T_{ref}, p_{ref}) \right] \quad (0.4.2)$$

0.4.1 Enthalpy of Formation - Example

In the following reactions:



Substance	Formula	Molar Mass, M (kg/kmol)	Enthalpy of Formation, \bar{h}_f° (kJ/kmol)	Gibbs Function of Formation, \bar{g}_f° (kJ/kmol)	Absolute Entropy, \bar{s}° (kJ/kmol · K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H ₂ (g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N ₂ (g)	28.01	0	0	191.50	—	—
Oxygen	O ₂ (g)	32.00	0	0	205.03	—	—
Carbon monoxide	CO(g)	28.01	−110,530	−137,150	197.54	—	—
Carbon dioxide	CO ₂ (g)	44.01	−393,520	−394,380	213.69	—	—
Water	H ₂ O(g)	18.02	−241,820	−228,590	188.72	—	—
Water	H ₂ O(l)	18.02	−285,830	−237,180	69.95	—	—
Hydrogen peroxide	H ₂ O ₂ (g)	34.02	−136,310	−105,600	232.63	—	—
Ammonia	NH ₃ (g)	17.03	−46,190	−16,590	192.33	—	—
Oxygen	O(g)	16.00	249,170	231,770	160.95	—	—
Hydrogen	H(g)	1.008	218,000	203,290	114.61	—	—
Nitrogen	N(g)	14.01	472,680	455,510	153.19	—	—
Hydroxyl	OH(g)	17.01	39,460	34,280	183.75	—	—
Methane	CH ₄ (g)	16.04	−74,850	−50,790	186.16	55,510	50,020
Acetylene	C ₂ H ₂ (g)	26.04	226,730	209,170	200.85	49,910	48,220
Ethylene	C ₂ H ₄ (g)	28.05	52,280	68,120	219.83	50,300	47,160
Ethane	C ₂ H ₆ (g)	30.07	−84,680	−32,890	229.49	51,870	47,480
Propylene	C ₃ H ₆ (g)	42.08	20,410	62,720	266.94	48,920	45,780
Propane	C ₃ H ₈ (g)	44.09	−103,850	−23,490	269.91	50,350	46,360
Butane	C ₄ H ₁₀ (g)	58.12	−126,150	−15,710	310.03	49,500	45,720
Pentane	C ₅ H ₁₂ (g)	72.15	−146,440	−8,200	348.40	49,010	45,350
Octane	C ₈ H ₁₈ (g)	114.22	−208,450	17,320	463.67	48,260	44,790
Octane	C ₈ H ₁₈ (l)	114.22	−249,910	6,610	360.79	47,900	44,430
Benzene	C ₆ H ₆ (g)	78.11	82,930	129,660	269.20	42,270	40,580
Methyl alcohol	CH ₃ OH(g)	32.04	−200,890	−162,140	239.70	23,850	21,110
Methyl alcohol	CH ₃ OH(l)	32.04	−238,810	−166,290	126.80	22,670	19,920
Ethyl alcohol	C ₂ H ₅ OH(g)	46.07	−235,310	−168,570	282.59	30,590	27,720
Ethyl alcohol	C ₂ H ₅ OH(l)	46.07	−277,690	174,890	160.70	29,670	26,800

Figure 6: Table A-25 — Thermochemical Properties of Selected Substances at 298K and 1 atm

0.4.2 Evaluating Enthalpy of Ideal Gases

Enthalpy of any ideal gas i at temperature T (independent of P):

$$\bar{h}_i(T) = \bar{h}_{f,i}^\circ + [\bar{h}_i(T) - \bar{h}_i(T_{ref})] \quad (0.4.6)$$

$$\text{Absolute enthalpy} = \text{Enthalpy of formation} + \text{Sensible enthalpy} \quad (0.4.7)$$

- Enthalpy of formation from its elements (see Table A-25 in text book)
- Enthalpy change from reference temperature of 298.15 K
 1. Evaluated from ideal gas Table A-22, A-23 in text book OR
 2. By calculation:

$$\Delta \bar{h}_i(T) = \bar{h}_i(T) - \bar{h}_i(T_{ref}) = \int_{298.15K}^T \bar{C}_p dT \quad (0.4.8)$$

0.5 Closed System Energy Analysis of Combustion

Closed Systems:

In the absence of kinetic and potential energy changes as well as mechanical work, the energy balance equation can be written as:

$$Q + \mathcal{W} = \Delta U_{CM} + \Delta KE_{CM} + \Delta PE_{CM} \quad (0.5.1)$$

$$Q = U_P - U_R \quad (0.5.2)$$

$$Q = \sum_P n_i \bar{u}_i - \sum_R n_i \bar{u}_i \quad (0.5.3)$$

$$Q = \sum_P n_i \left(\bar{h}_i - R_u T \right) - \sum_R n_i \left(\bar{h}_i - R_u T \right) \quad (0.5.4)$$

$$Q = \sum_P n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i - R_u T \right) - \sum_R n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i - R_u T \right) \quad (0.5.5)$$

0.6 Heat of Reaction

The **heat of reaction** (or **heat of combustion** or **chemical heat release**) is the energy released by the oxidation of a fuel under a specified (constant) temperature.

The heat of reaction is therefore measured by **keeping the temperature of the reactants and products the same**. It is also dependent on the process (or path) by which it is measured.

In a constant-volume process, the **heat of reaction** is the internal energy change, called **the internal energy of reaction**:

$$(Q_r)_{T,V} = (\Delta U_r)_{T,V} = U_P - U_R = \sum_P n_i \bar{u}_i(T) - \sum_R n_i \bar{u}_i(T) \quad (0.6.1)$$

$$= \sum_P n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i(T) - R_u T \right) - \sum_R n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i(T) - R_u T \right) \quad (0.6.2)$$

In a constant-pressure process, the **heat of reaction** is the enthalpy change, called **the enthalpy of reaction**.

$$(Q_r)_{T,P} = (\Delta H_r)_{T,P} = H_P - H_R = \sum_P n_i \bar{h}_i(T) - \sum_R n_i \bar{h}_i(T) \quad (0.6.3)$$

$$= \sum_P n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i(T) \right) - \sum_R n_i \left(\bar{h}_{f,i}^\circ + \Delta \bar{h}_i(T) \right) \quad (0.6.4)$$

$\Delta U_r, \Delta H_r < 0$ for exothermic reaction

$\Delta U_r, \Delta H_r > 0$ for endothermic reaction

0.6.1 Heat Release of Reaction between Arbitrary Temperatures

In reality, reactants and products are rarely at the same temperature, not to mention the reference temperature.

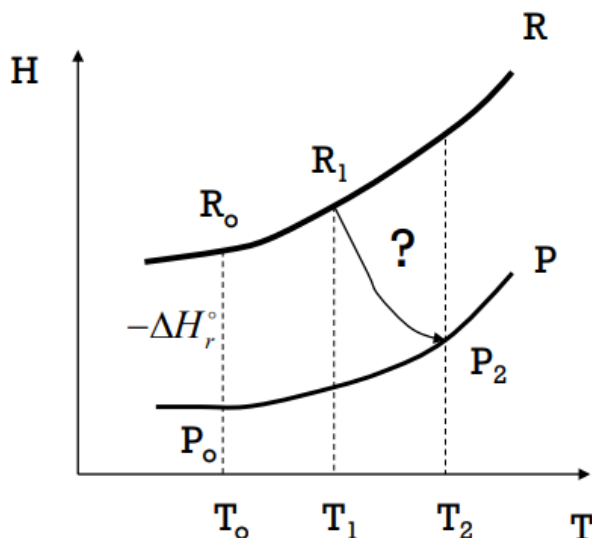


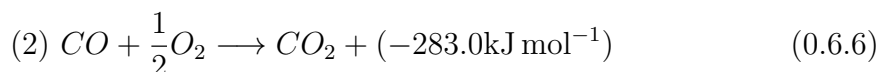
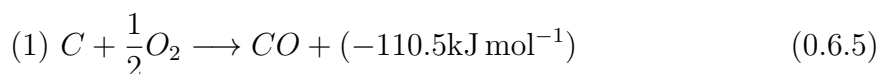
Figure 7:

0.6.2 Hess's Law

The enthalpy of reaction for a given reaction is the same whether it takes one or several stages to form the same product.

That is, the enthalpy of reaction is independent of the path of the reaction, but only dependent on the initial and final states.

For example:



is equivalent to:



0.6.3 Heat Release of Reaction between Arbitrary Temperatures

For a reaction of reactants at T_1 and products at T_2 , the enthalpy of reaction can be determined as follows:

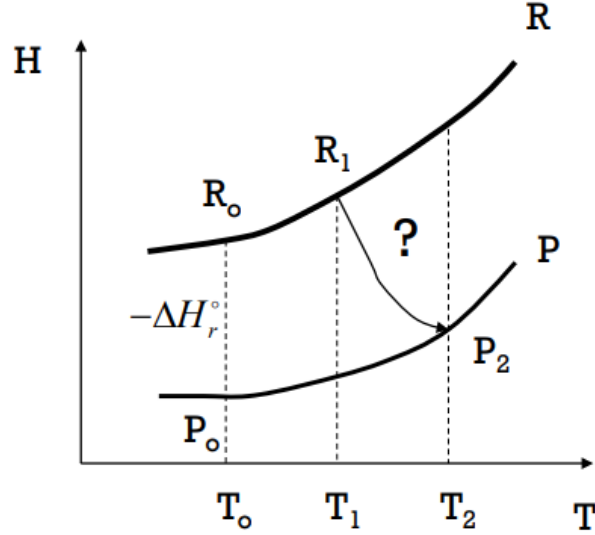


Figure 8:

$$(Q_r)_{T_1, T_2} = \Delta H_{T_1}^{T_2} = H_P(T_2) - H_R(T_1) \quad (0.6.8)$$

$$= H_P(T_2) - H_P(T_o) + H_P(T_o) - H_R(T_o) + H_R(T_o) - H_R(T_1) \quad (0.6.9)$$

On a mass basis:

$$= \sum_P \int_{T_o}^{T_2} m_i C_{p,i} dT + \Delta H_r^o + \sum_R \int_{T_1}^{T_o} m_i C_{p,i} dT \quad (0.6.10)$$

On a molar basis:

$$= \sum_P \int_{T_o}^T T_2 n_i \bar{C}_{p,i} dT + \Delta \bar{H}_r^o + \sum_R \int_{T_1}^{T_o} n_i \bar{C}_{p,i} dT \quad (0.6.11)$$

The enthalpy of reaction at standard reference conditions:

$$\Delta H_r^o = \sum_P m_i h_{f,i}^o - \sum_R m_i h_{f,i}^o \quad (0.6.12)$$

$$\text{OR} \quad (0.6.13)$$

$$\Delta \bar{H}_r^o = \sum_P n_i \bar{h}_{f,i}^o - \sum_R n_i \bar{h}_{f,i}^o \quad (0.6.14)$$

0.6.4 State of Water in Combustion Products

Water may exist as liquid or vapour in combustion products, depending on pressure and temperature.

Relationship between vapour phase and liquid phase enthalpies is given by:

$$\left(\Delta h_f^o \right)_{H_2O, vapour} = \left(\Delta h_f^o \right)_{H_2O, liquid} + (\Delta h_{fg})_{H_2O} \quad (0.6.15)$$

$$\left(\Delta \bar{h}_f^o \right)_{H_2O, vapour} = \left(\Delta \bar{h}_f^o \right)_{H_2O, liquid} + \left(\Delta \bar{h}_{fg} \right)_{H_2O} \quad (0.6.16)$$

Where $(\Delta h_{fg})_{H_2O}$ and $(\Delta \bar{h}_{fg})_{H_2O}$ are the enthalpy of evaporation in J kg^{-1} water and J kmol^{-1} , respectively.

Note that in text books, Δh_f° and h_f° are used interchangeably.

0.7 Heating Values of Fuels

The heating value of a fuel is the magnitude of heat of reaction of a unit composite fuel usually measured in a calorimeter under standard reference conditions (298.15K, 1 atm).

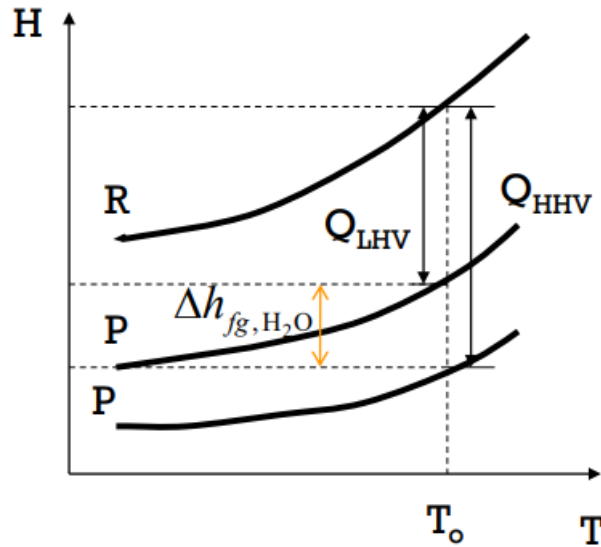


Figure 9:

1. The fuel composition is usually unknown;
2. The heating value is also called the calorific value;
3. HHV - higher heating value;
4. LHV – lower heating value;
5. h_{fg,H_2O} - enthalpy of evaporation;
6. For constant volume, $Q_{HV} = |\Delta U_r|$
7. For constant pressure, $Q_{HV} = |\Delta H_r|$

$$Q_{HHV} = Q_{LHV} + n_{H_2O} \Delta \bar{h}_{fg,H_2O} \longrightarrow (\text{J kmol}^{-1}) \quad (0.7.1)$$

$$Q_{HHV} = Q_{LHV} + m_{H_2O} \Delta h_{fg,H_2O} \longrightarrow (\text{J kg}^{-1}) \quad (0.7.2)$$

The values for HHV and LHV for specific substances can be found from Table A-25 — Thermochemical Properties of Selected Substances at 298K and 1 atm.

0.8 Adiabatic Flame Temperature

If all heat evolved during the reaction is used **solely** for raising the products temperature without heat loss, the final temperature T_2 is called the adiabatic flame temperature T_F .

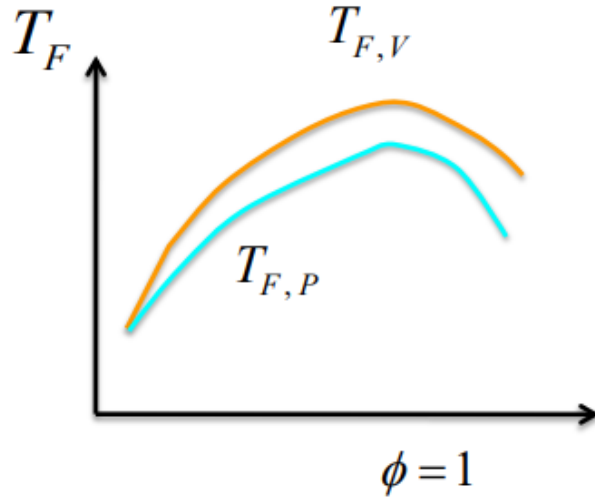


Figure 10:

The adiabatic flame temperature is obtained by setting:

$$\Delta \bar{H}_{T_1, r}^{T_2} = 0 \quad (0.8.1)$$

And solving the following equation iteratively,

$$\sum_P \int_{T_o}^{T_2} n_i \bar{C}_{p,i} dT + \sum_R \int_{T_1}^{T_o} n_i \bar{C}_{p,i} dT = -\Delta \bar{H}_r^\circ \quad (0.8.2)$$

$T_{F,P}$ is constant-pressure adiabatic flame temperature.

$T_{F,V}$ is constant-volume adiabatic flame temperature.