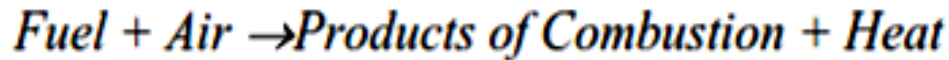


Combustion of Fuels:

Combustion of fuel is accomplished by mixing fuel with air at elevated temperature:



It is usual in combustion calculations to take air as 23.3% O_2 , 76.7% N_2 by mass, and 21% O_2 , 79% N_2 by volume.

So, based on the volumetric combustion analysis with one mole of O_2 there are $\frac{79}{21} = 3.76$ of N_2 .

A frequently used quantity in the analysis of combustion process is the *air-fuel ratio* A/F. it is defined as the ratio of the mass of air to the mass of fuel for a combustion process.

$$A/F = \frac{m_a}{m_f} = \frac{\text{mass of air}}{\text{mass of fuel}}$$

The mass m of a substance is related to the number of moles n through the relation: $m = nM$, where M is the *molar mass*. The reciprocal of A/F ratio is called the *fuel-air ratio*.

The molar mass of O_2 can be taken as 32 kg/kmol, and that of N_2 as 28 kg/kmol and air 29 kg/kmol.

The minimum amount of air needed for the complete combustion of a fuel is called the stoichiometric or theoretical air. In actual combustion processes, it is common practice to use more air than the stoichiometric amount. The amount of extra air than the stoichiometric is called (*excess air*). Amount of air less than stoichiometric amount is called (*deficiency of air*). *Equivalence ratio* is the ratio of the actual fuel- air ratio to the stoichiometric fuel-air ratio. Sometimes this ratio is given in term of A/F ratio and called *mixture strength*.

$$\text{Mixture strength} = \frac{\text{Stoichiometric A/F Ratio}}{\text{Actual A/F Ratio}}$$

$$\text{Equivalence ratio} = \frac{\text{Actual (F/A) ratio}}{\text{Stoich. (F/A) ratio}} = \phi$$

Where:

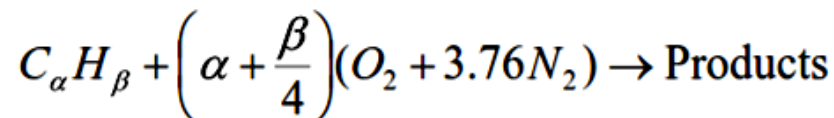
$$\phi = \frac{(\text{F/A})_{\text{actual}}}{(\text{F/A})_{\text{stoich}}} = \frac{(\text{A/F})_{\text{stoich}}}{(\text{A/F})_{\text{actual}}}$$

$\phi = 1$: stoichiometric

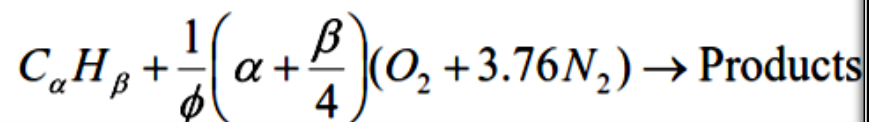
$\phi < 1$: lean (weak) mixture- excess of air.

$\phi > 1$: rich mixture- deficiency of air.

Stoichiometric mixture:



Off-stoichiometric mixture:

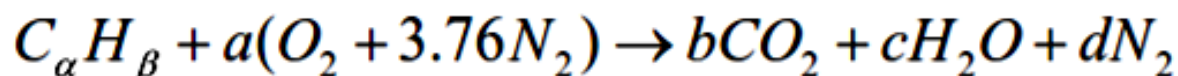


λ : is the excess or relative ratio = $\frac{1}{\phi}$

Combustion Stoichiometry

Air contains molecular nitrogen N_2 , if products are at a “low” temperature the nitrogen is not significantly affected by the reaction, it is considered inert.

The complete reaction of a general hydrocarbon $C_\alpha H_\beta$ with air is:

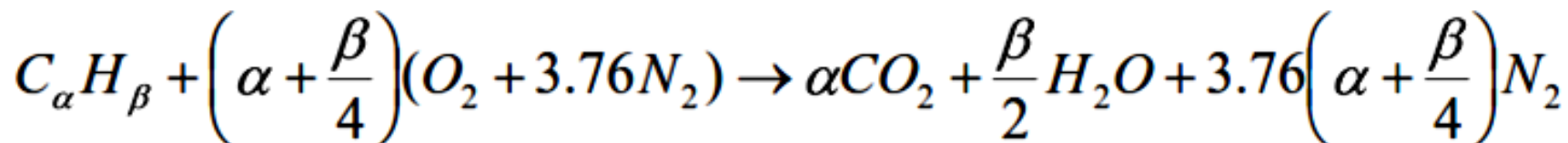


C balance: $\alpha = b \rightarrow b = \alpha$

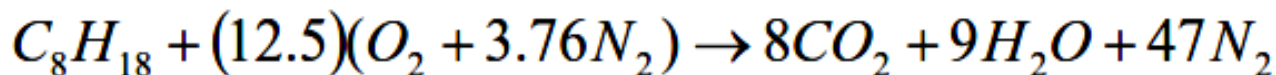
H balance: $\beta = 2c \rightarrow c = \beta/2$

O balance: $2a = 2b + c \rightarrow a = b + c/2 \rightarrow a = \alpha + \beta/4$

N balance: $2(3.76)a = 2d \rightarrow d = 3.76a/2 \rightarrow d = 3.76(\alpha + \beta/4)$



Example: The stoichiometric reaction of octane (C_8H_{18}) $\alpha = 8$ and $\beta = 18$



Combustion Stoichiometry

The stoichiometric mass based air/fuel ratio for $C_\alpha H_\beta$ fuel is:

$$(A/F)_s = \frac{m_{air}}{m_{fuel}} = \frac{(\sum n_i \bar{M}_i)_{air}}{(\sum n_i \bar{M}_i)_{fuel}} = \frac{\left(\alpha + \frac{\beta}{4}\right) \bar{M}_{O_2} + 3.76 \left(\alpha + \frac{\beta}{4}\right) \bar{M}_{N_2}}{\alpha \bar{M}_C + \beta \bar{M}_H}$$

Substituting the respective molecular weights and dividing top and bottom by α one gets the following expression that only depends on the ratio of the number of hydrogen atoms to carbon atoms (β/α) in the fuel.

$$(A/F)_s = \frac{1}{(F/A)_s} = \frac{\left(1 + \frac{(\beta/\alpha)}{4}\right)(32 + 3.76 \cdot 28)}{12 + (\beta/\alpha) \cdot 1} = \frac{137.28 \left(1 + \frac{(\beta/\alpha)}{4}\right)}{12 + (\beta/\alpha)}$$

Note above equation only applies to stoichiometric mixture

Example: For octane (C_8H_{18}), $\beta/\alpha = 2.25 \rightarrow (A/F)_s = 15.1$

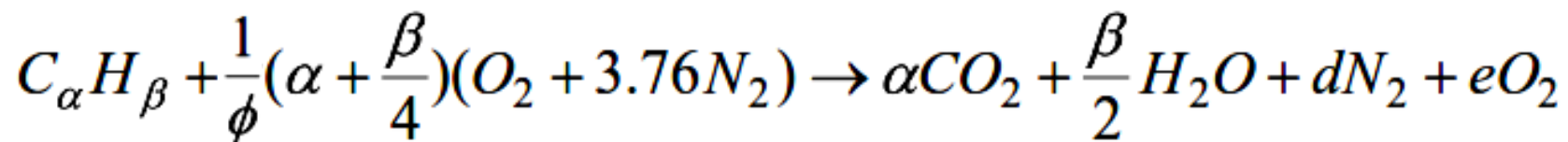
(gasoline $(A/F)_s \approx 14.6$)

Fuel Lean Mixture

Fuel-air mixtures with more than stoichiometric air (excess air) can burn

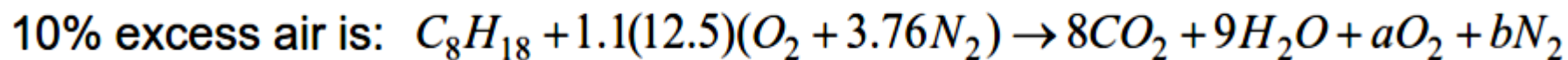
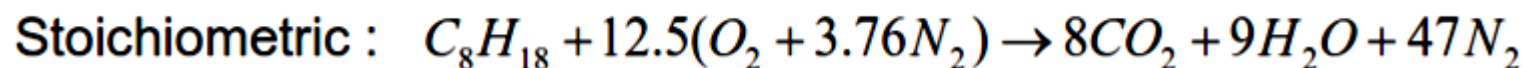
With excess air you have fuel lean combustion $(\lambda > 1)$

At low combustion temperatures, the extra air appears in the products as O_2 and N_2 :



Above reaction equation has two unknowns (d, e) and we have two atom balance equations (O, N) so can solve for the unknowns

Example: Consider a reaction of octane with 10% excess air, what is ϕ ?



O balance: $1.1(12.5)(2) = 16 + 9 + 2a \rightarrow a = 1.25,$

N balance: $1.1(12.5)(3.76)(2) = 2b \rightarrow b = 51.7$

$$\phi = \frac{(A/F)_s}{(A/F)_{mixture}} = \frac{12.5(4.76)/1}{1.1(12.5)(4.76)/1} = 0.91$$

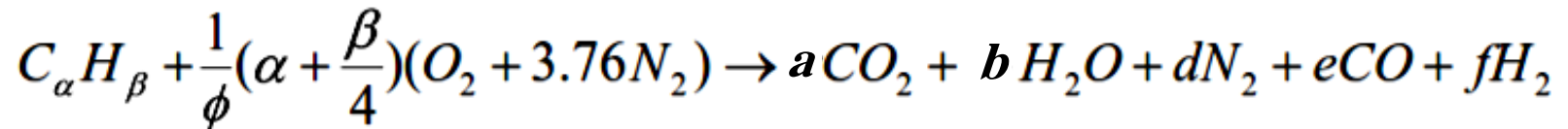
Fuel Rich Mixture

$$(\lambda < 1)$$

Fuel-air mixtures with less than stoichiometric air (excess fuel) can burn.

With less than stoichiometric air you have fuel rich combustion, there is insufficient oxygen to oxidize all the C and H in the fuel to CO_2 and H_2O .

Get incomplete combustion where carbon monoxide (CO) and molecular hydrogen (H_2) also appear in the products.



Above reaction equation has five unknowns (a, b, d, e, f) and we only have four atom balance equation (C, H, O, N), so cannot solve for the unknowns unless additional information about the products is given.

If the product species CO_2 , H_2O , CO and H_2 are at equilibrium, an additional equation can be obtained from the water-gas reaction: $CO_2 + H_2 \leftrightarrow CO + H_2O$

The equilibrium constant for this reaction provides the fifth equation:

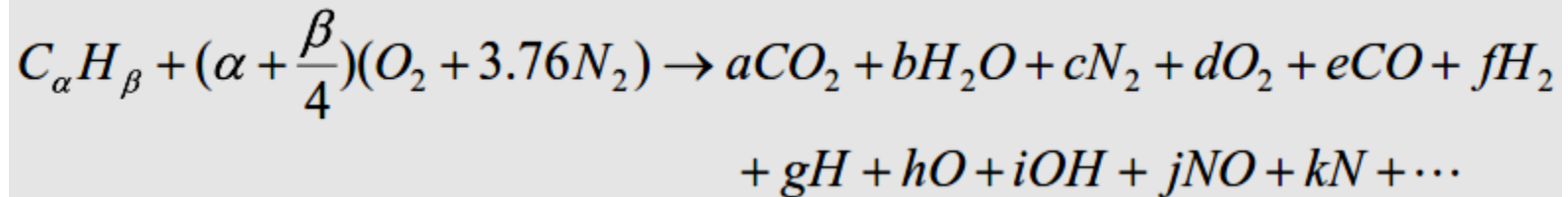
$$K(T) = \frac{Y_{CO} \cdot Y_{H_2O}}{Y_{CO_2} \cdot Y_{H_2}} = \frac{e \cdot b}{a \cdot f} \quad P = 1 \text{ atm} \quad Y_i = \frac{n_i}{\sum_{i=1}^j n_i} \quad \text{for } i = 1, 2, 3, \dots, j.$$

Note K is tabulated as a function of T

Major and minor species of combustion products

Major products of lean combustion are H_2O , CO_2 , O_2 and N_2 ; while, for rich combustion these are H_2O , CO_2 , CO , H_2 and N_2 .

If the products are at high temperature ($>2000K$) minor species will be present due to the dissociation of the major species CO_2 , H_2O , N_2 and O_2 .

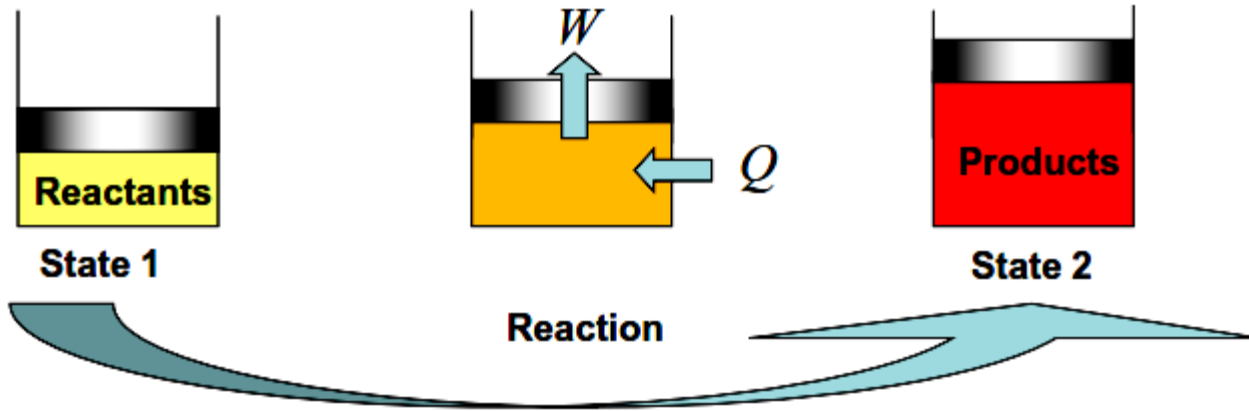
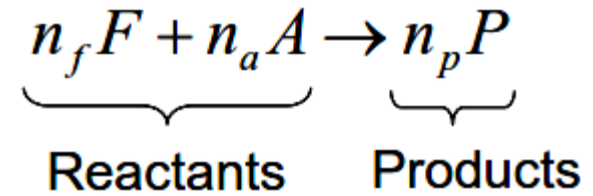


Exhaust and Flue Gas Analysis:

The products of combustion are mainly gaseous. When a sample is taken for analysis it is usually cooled down to a temperature which is below the saturation temperature of the steam present. The steam content is therefore not included in the analysis, which is then quoted as the analysis of *dry products*. Since the products are gaseous, it is usual to quote the analysis by volume. An analysis which includes the steam in the exhaust is called a *wet analysis*.

First Law Analysis for Reacting System

Consider a constant pressure process in which n_f moles of fuel react with n_a moles of air to produce n_p moles of product:



Applying First Law with state 1 being the reactants at P_1, T_1 and state 2 being products at P_2, T_2 :

$$Q = \Delta U + W$$

$$Q_{1 \rightarrow 2} = (U_2 - U_1) + P(V_2 - V_1) = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

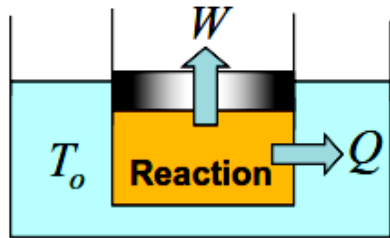
$$= H_2 - H_1 = H_P - H_R$$

$$Q = \sum_P n_i \bar{h}_i(T_P) - \sum_R n_i \bar{h}_i(T_R)$$

Enthalpy of Reaction

Consider the case where the final temperature of the products is the same as the initial temperature of the reactants (e.g., calorimeter is used to measure Q).

The heat release under this situation is referred to the **enthalpy of reaction**, ΔH_R



$$Q = \Delta H_R \quad \Delta H_R = H_P - H_R < 0 \text{ (exothermic)}$$

$$P_1 = P_2 = P_o \quad = \sum_P n_i \bar{h}_i(T_P) - \sum_R n_i \bar{h}_i(T_R)$$

$$T_1 = T_2 = T_o \quad = \sum_P n_i \bar{h}_i(T_o) - \sum_R n_i \bar{h}_i(T_o) \quad \text{units: kJ per kg or kmol of fuel}$$

Heat of Formation

$$\Delta H_R = H_P - H_R > 0 \text{ (endothermic)}$$

Consider the following reactions taking place at atmospheric pressure and with $T_P = T_R = 298\text{K}$



In these reactions H_2O and CO_2 are formed from their elements in their natural state at standard temperature and pressure (STP) 1 atm and 298K.

Reactions of this type are called formation reactions and the corresponding measured heat release Q is referred to as the standard heat of formation

(\bar{h}_f^o) so:

$$\bar{h}_{f, H_2O}^o = \bar{Q} = -286,000 \text{ kJ / kmol} \quad \bar{h}_{f, CO_2}^o = \bar{Q} = -394,000 \text{ kJ / kmol}$$

Enthalpy of formation at 25°C and 1 atm.

<i>Substance</i>	<i>Formula</i>	\bar{h}_f° (MJ/kmol)	<i>Substance</i>	<i>Formula</i>	\bar{h}_f° (MJ/kmol)
Carbon monoxide	CO(g)	-110.52	Cetane	C ₁₆ H ₃₄ (l)	-45.45
Carbon dioxide	CO ₂ (g)	-393.52	Acetylene	C ₂ H ₂ (g)	+226.87
Water	H ₂ O(l)	-285.8	Ethene	C ₂ H ₄ (g)	+52.32
Water	H ₂ O(g)	-241.82	Propylene	C ₃ H ₆ (g)	+20.41
Methane	CH ₄ (g)	-74.87	Benzene	C ₆ H ₆ (g)	+82.98
Ethane	C ₂ H ₆ (g)	-84.68	Methanol	CH ₃ OH(g)	-201.17
Propane	C ₃ H ₈ (g)	-103.85	Methanol	CH ₃ OH(l)	-238.58
Butane	C ₄ H ₁₀ (g)	-126.22	Ethanol	C ₂ H ₅ OH(g)	-208.45
Isooctane	C ₈ H ₁₈ (g)	-224.1	Ethanol	C ₂ H ₅ OH(l)	-249.35
Isooctane	C ₈ H ₁₈ (l)	-259.28	Ammonia	NH ₃ (g)	-45.93
<i>n</i> -Octane	C ₈ H ₁₈ (g)	-208.58	Hydrazine	N ₂ H ₄ (g)	+95.41
<i>n</i> -Octane	C ₈ H ₁₈ (l)	-250.10	Hydrogen peroxide	H ₂ O ₂ (g)	-136.31
Dodecane	C ₁₂ H ₂₆ (g)	-290.97			

Enthalpy Scale for a Reacting System

By international convention, the enthalpy of every element in its natural state (e.g., $O_2(g)$, $N_2(g)$, $H_2(g)$, $C(s)$) at STP has been set to zero

$$\text{i.e., } \bar{h}(1\text{atm}, 298\text{K}) = \bar{h}_f^\circ = 0$$

Consider the following identity:

$$\bar{h}(P, T) = \bar{h}(1\text{atm}, 298\text{K}) + [\bar{h}(P, T) - \bar{h}(1\text{atm}, 298\text{K})]$$

Therefore, the enthalpy of the i 'th component in a mixture is:

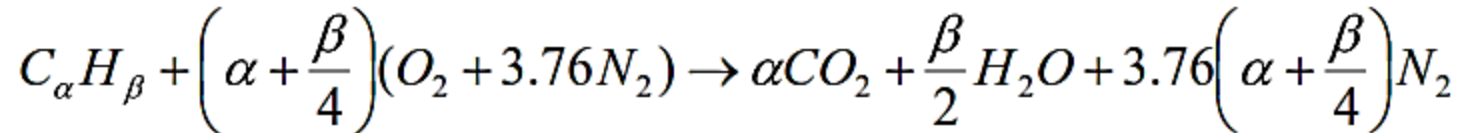
$$\bar{h}_i(P, T) = \underbrace{\bar{h}_{f,i}^\circ}_{\text{chemical enthalpy 298K}} + \underbrace{[\bar{h}_i(P, T) - \bar{h}_i(1\text{atm}, 298\text{K})]}_{\text{sensible enthalpy}} = \int_{298\text{K}}^T c_{p,i} dT$$

Change in enthalpy ($\bar{h}^{\circ} - \bar{h}_{298}^{\circ}$) between the reference state and the actual state for different substances (MJ/kmol)

Temp, T (K)	CO	CO ₂	H ₂ O	N ₂	O ₂
0	-8.669	-9.364	-9.904	-8.669	-8.682
100	-5.770	-6.456	-6.615	-5.770	-5.778
200	-2.858	-3.414	-3.280	-2.858	-2.866
298	0.000	0.000	0.000	0.000	0.000
300	0.054	0.067	0.063	0.054	0.054
400	2.975	4.008	3.452	2.971	3.029
500	5.929	8.314	6.920	5.912	6.088
600	8.941	12.916	10.498	8.891	9.247
700	12.021	17.761	14.184	11.937	12.502
800	15.175	22.815	17.991	15.046	15.841
900	18.397	28.041	21.924	18.221	19.246
1000	21.686	33.405	25.978	21.460	22.707
1100	25.033	38.894	30.167	24.757	26.217
1200	28.426	44.484	34.476	28.108	29.765
1300	31.865	50.158	38.903	31.501	33.351
1400	35.338	55.907	43.447	34.936	36.966
1500	38.848	61.714	48.095	38.405	40.610
1600	42.384	67.580	52.844	41.903	44.279
1700	45.940	73.492	57.685	45.430	47.970
1800	49.522	79.442	62.609	48.982	51.689
1900	53.124	85.429	67.613	52.551	55.434

Heat of Combustion

The maximum amount of energy is released from a fuel when reacted with a stoichiometric amount of air and all the hydrogen and carbon contained in the fuel is converted to CO_2 and H_2O



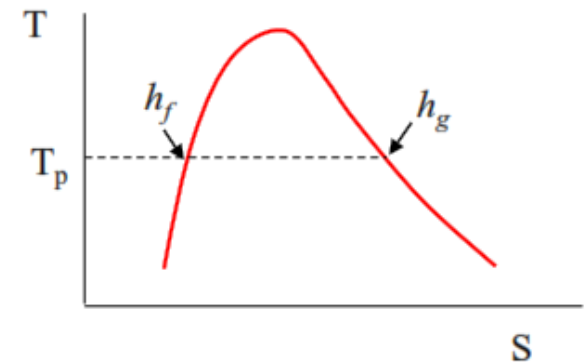
This maximum energy is commonly referred to as the heat of combustion, or the heating value, given per unit mass of fuel or air

$$\Delta H_R = H_P - H_R < 0 \text{ (exothermic)} \quad \Delta H_R = H_P - H_R > 0 \text{ (endothermic)}$$

There are two possible values for the heat of combustion depending on whether the water in the products is taken to be saturated liquid or vapour.

The term **higher heat of combustion** and **heating value (HHV)** is used when the water in the products is taken to be in the liquid state ($h_{\text{H}_2\text{O}} = h_f$)

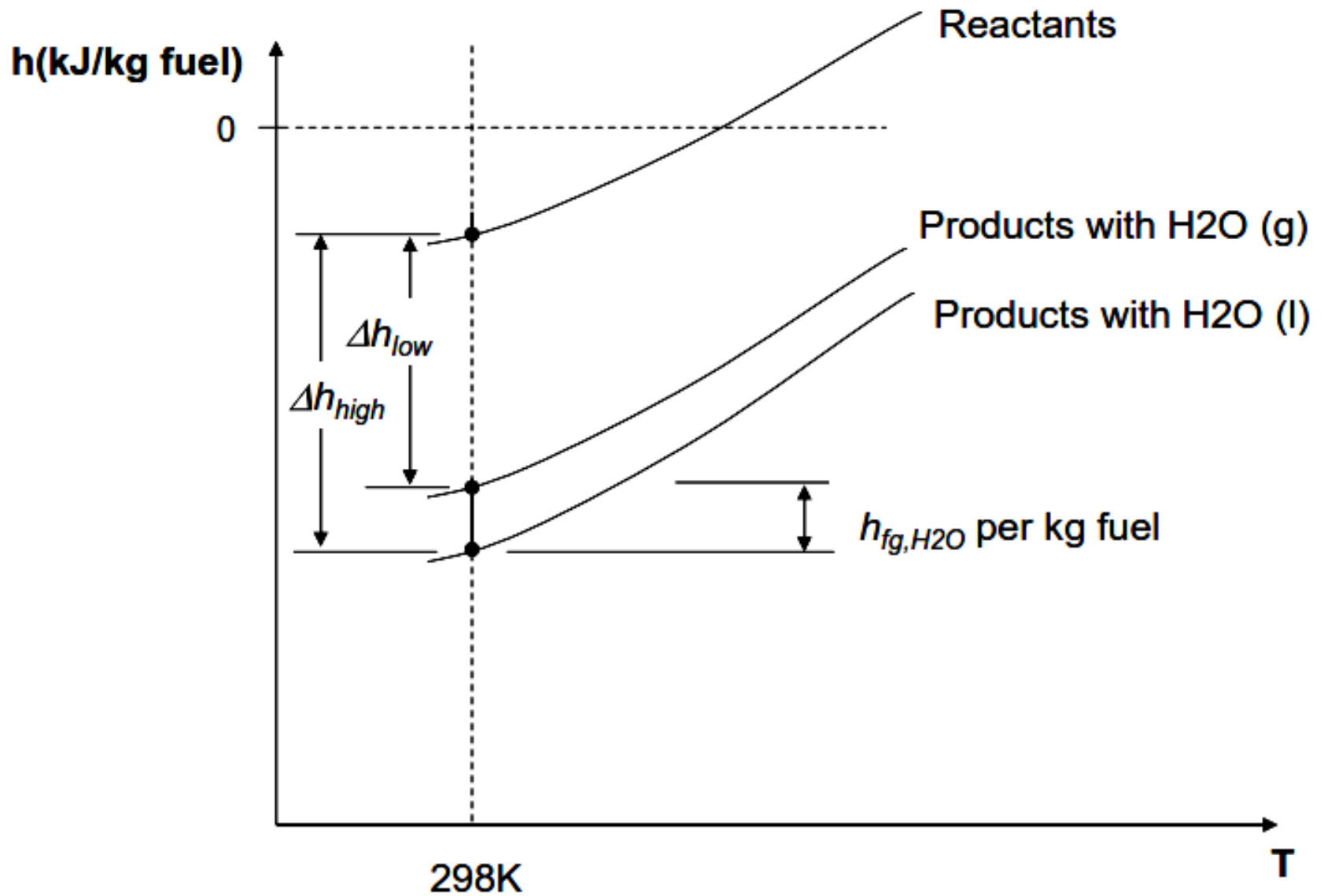
The term **lower heat of combustion** and **heating value (LHV)** is used when the water in the products is taken to be in the vapor state ($h_{\text{H}_2\text{O}} = h_g$)



From steam tables:

$$h_{fg} = h_g - h_f > 0$$

Heat of Combustion, graphical



Internal Energy of Combustion

The internal energy of combustion, ΔU , is the difference between the internal energy of products and the internal energy of the reactants, when complete combustion of unit quantity of fuel occurs at a given temperature and volume. That is,

$$\Delta U = U_P - U_R = [H - pV]_P - [H - pV]_R \quad H = U + pV$$

$$\therefore \Delta U = \sum_P n_j [\bar{h}_f^\circ + (\bar{h}_T^\circ - \bar{h}_{298}^\circ) - p\bar{v}]_j - \sum_R n_i [\bar{h}_f^\circ + (\bar{h}_T^\circ - \bar{h}_{298}^\circ) - p\bar{v}]_i$$

If all the products and reactants are gases, $p\bar{v} = \bar{R}T$

$$\Delta U = \sum_P n_j [\bar{h}_f^\circ + (\bar{h}_T^\circ - \bar{h}_{298}^\circ) - \bar{R}T]_j - \sum_R n_i [\bar{h}_f^\circ + (\bar{h}_T^\circ - \bar{h}_{298}^\circ) - \bar{R}T]_i$$

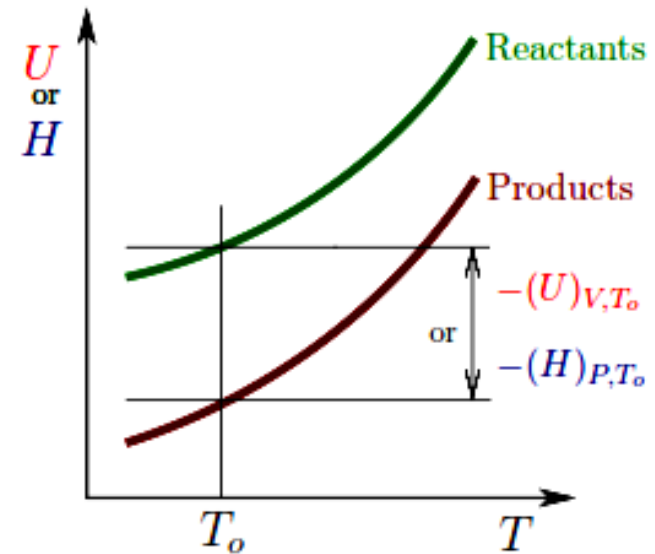
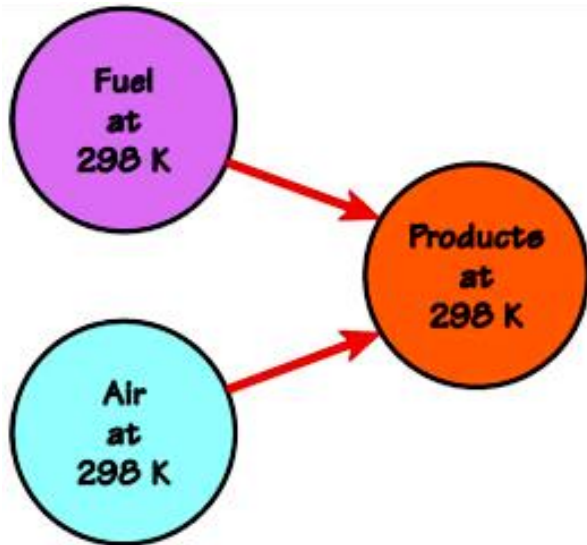
Accordingly, the following expression can be written to relate ΔU and ΔH :

$$\Delta U = \Delta H - \bar{R}T \left(\sum_P n_j - \sum_R n_i \right)$$

or
$$\Delta H = \Delta U + \Delta n \bar{R}T$$

where
$$\Delta n = \sum_P n_j - \sum_R n_i$$

Relation of Heating Value with ΔU and ΔH



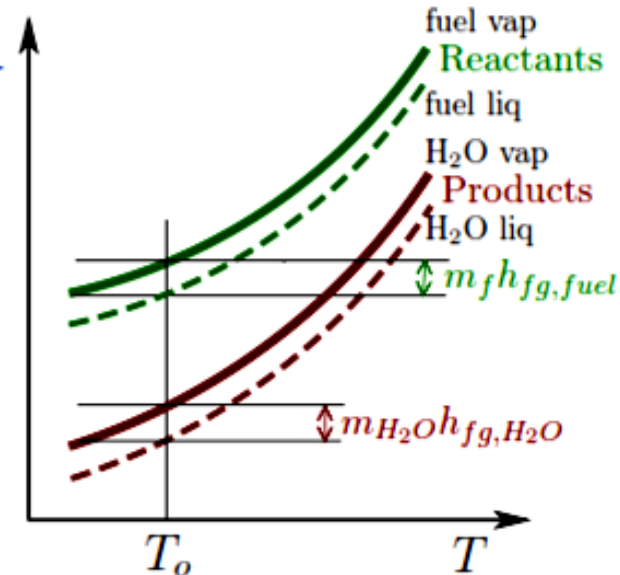
- Heating value at constant pressure $\equiv Q_{HV,P} = -(\Delta H)_{P,T_o}$
- Heating value at constant volume $\equiv Q_{HV,V} = -(\Delta U)_{V,T_o}$

$$Q_{HV,P} - Q_{HV,V} = -P(V_{prod} - V_{reac}) = -R_u(n_{prod} - n_{reac})T_o$$

$R_u \equiv$ universal gas constant (8.314 kJ/kmol-K)

$$Q_{HHV,P} = Q_{LHV,P} + \left[\frac{m_{H_2O}}{m_f} \right] h_{fg,H_2O}$$

- $Q_{HHV,P} \equiv$ Higher (Gross) Heating Value (water in liquid form)
- $Q_{LHV,P} \equiv$ Lower (Net) Heating Value (water in gaseous form)
- $m_{H_2O}/m_f \equiv$ mass ratio of water produced to fuel burned.



Adiabatic Flame Temperature is the product temperature in an ideal adiabatic combustion process. Actual peak temperatures in engines are several hundred degrees less due to:

- heat loss from the flame,
- combustion efficiency is less than 100%: a small fraction of fuel does not get burned, and some product components dissociate (endothermic reaction) at high temperatures.

Applying First Law with state 1 being the reactants at P_1, T_1 and state 2 being products at P_2, T_2 :

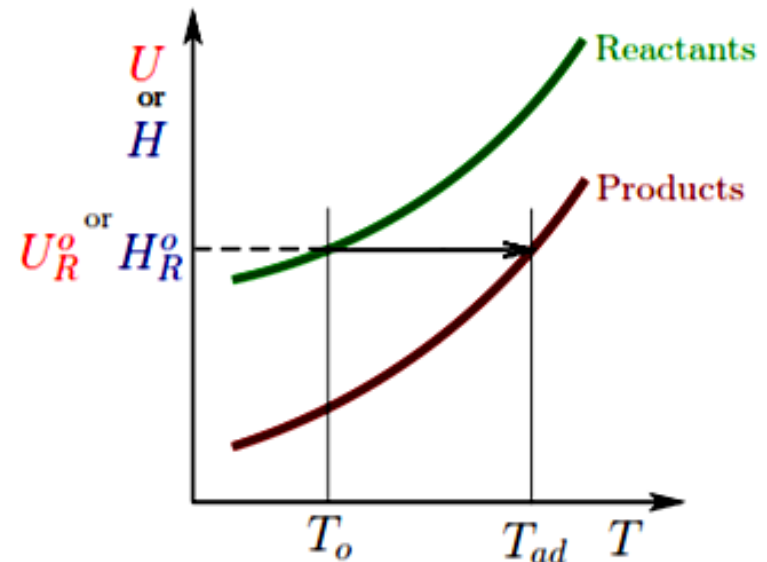
$$\begin{aligned} Q_{1 \rightarrow 2} &= (U_2 - U_1) + P(V_2 - V_1) \\ &= (U_2 + P_2V_2) - (U_1 + P_1V_1) \end{aligned}$$

For an adiabatic constant-volume combustion process, $Q = 0$:

$$U_R^o = U_{prod}(T_{ad}, V = \text{constant})$$

For an adiabatic constant-pressure combustion process, $Q = 0$:

$$H_R^o = H_{prod}(T_{ad}, P = \text{constant})$$



Combustion Efficiency in ICEs

In practice, the exhaust gas of an internal combustion engine contains incomplete combustion products (e.g., CO, H₂, unburned hydrocarbons, soot) as well as complete combustion products (CO₂ and H₂O).

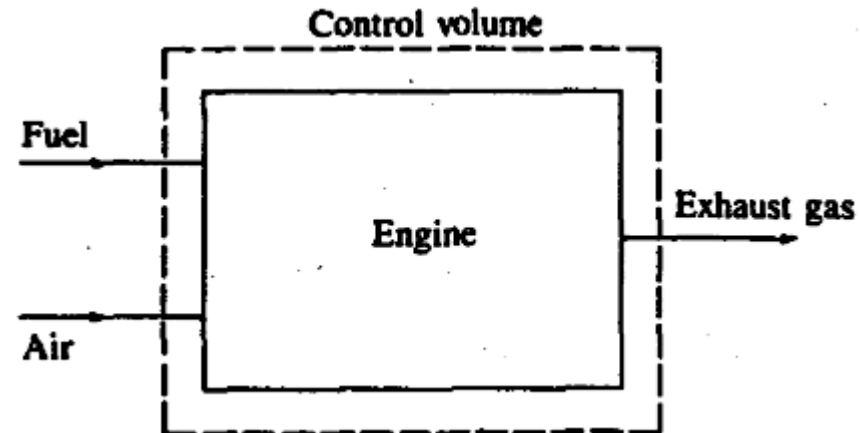
Because a fraction of the fuel's chemical energy is not fully released inside the engine during the combustion process, it is useful to define a **combustion efficiency**.

The engine can be analyzed as an open system which exchanges heat and work with its surrounding environment (the atmosphere), see Figure below:

- Reactants (fuel and air) flow into the system;
- Products (exhaust gases) flow out.
- Consider a mass m passes through the control volume surrounding engine.

The **net chemical energy release** due to combustion within the engine is given by:

$$[H_R(T_A) - H_P(T_A)] = m \left(\sum_{i, \text{ reactants}} n_i \Delta \tilde{h}_{f,i}^\circ - \sum_{i, \text{ products}} n_i \Delta \tilde{h}_{f,i}^\circ \right)$$



Combustion Efficiency in ICEs

$$[H_R(T_A) - H_P(T_A)] = m \left(\sum_{i, \text{ reactants}} n_i \Delta \tilde{h}_{f,i}^\circ - \sum_{i, \text{ products}} n_i \Delta \tilde{h}_{f,i}^\circ \right)$$

Enthalpy is the appropriate property, since $p_R = p_P = p_a$.

The amount of fuel energy supplied to the control volume around the engine which can be released by combustion is $\dot{m}_f \times Q_{HV}$.

Hence, the combustion efficiency is the fraction of the fuel energy supplied which is released in the combustion process-is given by:

$$\eta_c = \frac{H_R(T_A) - H_P(T_A)}{\dot{m}_f Q_{HV}}$$

Note that \dot{m} and \dot{m}_f could be replaced by the average mass flow rates \dot{m} and \dot{m}_f .

