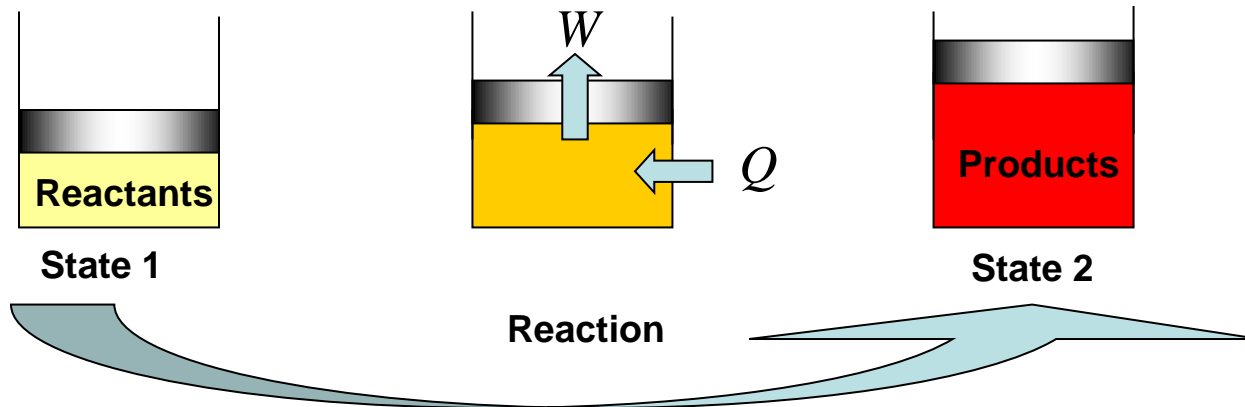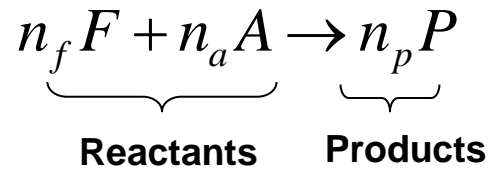# First Law Analysis for Reacting System

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:

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

Reactants **Products**

W

Q

Reactants

Products

State 1

State 2

Reaction

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

$$Q = \Delta U + W$$

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

First Law Analysis for Reacting System

$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

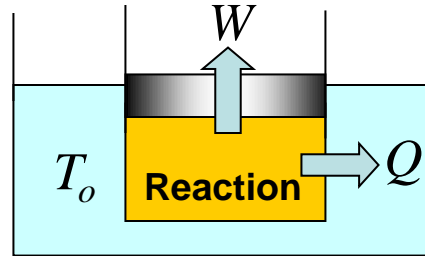$$= (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$= H_2 - H_1$$

$$= H_P - H_R = \sum_P n_i \bar{h}_i (T_p) - \sum_R n_i \bar{h}_i (T_R)$$

$H_P < H_R \qquad Q < 0 \qquad$ exothermic reaction

$H_P > H_R \qquad Q > 0 \qquad$ endothermic reaction

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).
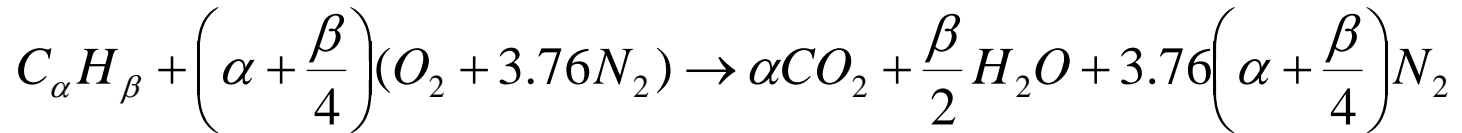

$$P_1 = P_2 = P_o$$
$$T_1 = T_2 = T_o$$

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

$$\Delta H_R = \sum_P n_i \bar{h}_i (T_p) - \sum_R n_i \bar{h}_i (T_R)$$

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

Heat of 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

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

This maximum energy is referred to as the **heat of combustion** or the **heating value** and it is typically given per mass of fuel

FUEL		$\Delta H_R(298K)\{MJ/kg\}$
C_2N_2 (g)	Cyanogen	21.0
H_2 (g)	Hydrogen	141.6
NH_3 (g)	Ammonia	22.5
CH_4 (g)	Methane	55.5
C_3H_9 (g)	Propane	50.3
C_8H_{19} (l)	Octane	47.9
$C_{15}H_{32}$ (l)	Pentadecane	47.3
$C_{20}H_{40}$ (g)	Eicosane	47.3
C_2H_2 (g)	Acetylene	49.9
$C_{10}H_8$ (s)	Naphthalene	40.3
CH_4O (l)	Methanol	22.7
C_2H_6O (l)	Ethanol	29.7
CH_3NO_2 (l)	Nitromethane	11.6

Heat of Combustion

There are two possible values for the heat of combustion that can be calculated depending on whether the water in the products is taken to be in a liquid or vapour state.
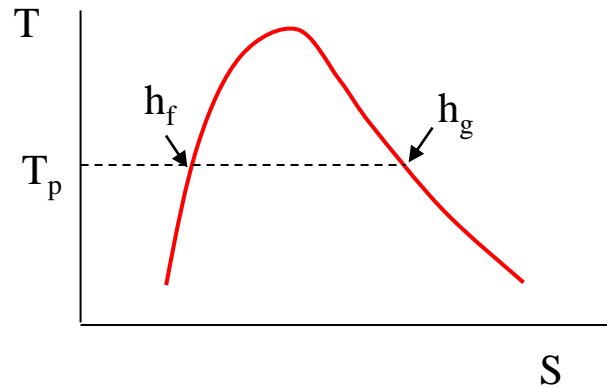
From steam tables:
$$h_{fg} = h_g - h_f > 0$$

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

The term **higher heat of combustion** is used when the water in the products is taken to be in the liquid state

The term **lower heat of combustion** is used when the water in the products is taken to be in the vapour state

Heat of Formation

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

$$1/2\,O_2(g) + H_2(g) \rightarrow H_2O(l) \qquad \overline{Q} = -286{,}000 \; kJ\,/\,kmol \; H_2O$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \overline{Q} = -394{,}000 \; kJ\,/\,kmol \; CO_2$$

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 $\overline{Q}$ is referred to as the **standard heat of formation** and takes the symbol $\overline{h}_f^{\,o}$ so:

$$\overline{h}_{f,\,H_2O}^{\,o} = -286{,}000 \; kJ\,/\,kmol$$

$$\overline{h}_{f,\,CO_2}^{\,o} = -394{,}000 \; kJ\,/\,kmol$$

Values for standard heat of formation for different species are tabulated

Enthalpy Scale for a Reacting System

We need to take into account that for a reacting system the working fluid changes molecularly from reactants to products while undergoing a process.

Consider the following identity:

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

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

$$\bar{h}(1atm, 298K) = \bar{h}^{o} = 0 \qquad \text{(note the notation convention)}$$

at STP

Enthalpy Scale for a Reacting System

The enthalpy of all other substances at STP is simply the heat of formation of the substance, since it is formed from its elements, for example:

$$1/2 O_2(g) + H_2(g) \rightarrow H_2O(l)$$
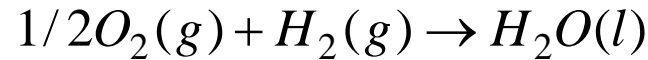
$$recall \; @ \; STP \quad Q = \bar{h}_{H_2O(l)} - 1/2 \cancel{\bar{h}}_{O_2(g)} - \cancel{\bar{h}}_{H_2(g)} \equiv \bar{h}_{f,H_2O(l)}$$

$$\rightarrow \bar{h}_{H_2O(l)} = \bar{h}_{f,H_2O(l)}$$

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

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

The sensible enthalpy for different species is tabulated as a function of temperature (JANNAF Tables).