Thermochemistry

is the study of the heat energy associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings.

Thermochemistry rests on two generalizations:

1. Lavoisier and Laplace's law (1780): The energy change accompanying any transformation is equal and opposite to energy change accompanying the reverse process.[2[
2. Hess' law (1840): The energy change accompanying any transformation is the same whether the process occurs in one step or many.

- Goal: To predict ΔH for every reaction, even if it cannot be carried out in the laboratory

The heat of reaction ΔH_{rx} is the ΔH for the *isothermal* reaction at constant pressure.

e.g. $Fe_2O_3(s,T,p) + 3H_2(g,T,p) = 2Fe(s,T,p) + 3H_2O(l,T,p)$

$$\Delta H_{rx}(T,p) = 2\bar{H}_{Fe}(T,p) + 3\bar{H}_{H_2O}(T,p) - 3\bar{H}_{H_2}(T,p) - \bar{H}_{Fe_2O_3}(T,p)$$

$$[\Delta H_{rx} = H(\text{products}) - H(\text{reactants})]$$

We cannot know $\bar{H}$ values because enthalpy, like energy, is not measured on an absolute scale. We can only measure differences in enthalpy.

$\bar{H}(298.15\text{K}, 1\text{ bar}) \equiv 0$ For every element in its most stable form at 1 bar and 298.15K

e.g.
$$\left.\begin{aligned}\bar{H}^\circ_{H_2(g)}(298.15K) &= 0\\ \bar{H}^\circ_{C(\text{graphite})}(298.15K) &= 0\end{aligned}\right\}$$
The "$\circ$" means 1 bar

- $\Delta H_f^\circ(298.15K)$: We can now write reactions to <u>form</u> every compound from its constituent atoms. The heat of reaction is the heat of formation of 1 mole of that compound from the constituent elements in their most stable forms.

<u>Example</u> (let T = 298.15 K)

$\frac{1}{2}$ H_2 (g, T,1 bar) + $\frac{1}{2}$ Br_2 (l, T,1 bar) = HBr (g, T,1 bar)

$$\Delta H_{rx} = \Delta \bar{H}_f^\circ(\text{products}) - \Delta \bar{H}_f^\circ(\text{reactants})$$
$$= \Delta \bar{H}_{f,HBr}^\circ(g,T) - \underbrace{\frac{1}{2}\Delta \bar{H}_{f,H_2}^\circ(g,T) - \frac{1}{2}\Delta \bar{H}_{f,Br_2}^\circ(l,T)}_{0\text{ - elements in most stable forms}} = \Delta \bar{H}_{f,HBr}^\circ(g,T)$$

We can <u>calculate</u> $\Delta \bar{H}_{rx}^\circ(T)$ for any reaction (T = 298.15K).

e.g.

CH_4 (g, T,1 bar) + $2O_2$ (g, T,1 bar) = CO_2 (g, T,1 bar) + $2H_2O$(l, T, 1 bar)

- First decompose reactants into elements
- Second put elements together to form products
- Use Hess's law [A statement of the fact that because H is a function of state, we can add ΔH's around paths.]

CH_4 (g, T,1 bar) = $C_{graphite}$ (s, T,1 bar) + $2H_2$(g, T,p)	ΔH_{I}
$2O_2$ (g, T,1 bar) = $2O_2$ (g, T,1 bar)	ΔH_{II}
$C_{graphite}$ (s, T,1 bar) + O_2 (g, T,1 bar) = CO_2 (g, T,1 bar)	ΔH_{III}
$2H_2$(g, T,p) + O_2 (g, T,1 bar) = $2H_2O$(l, T, 1 bar)	ΔH_{IV}

CH_4 (g, T,1 bar) + $2O_2$ (g, T,1 bar) = CO_2 (g, T,1 bar) + $2H_2O$(l, T, 1 bar)

$$\Delta H_{rx} = \Delta H_{I} + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV}$$

$$\Delta H_{I} = \bar{H}_{C} + 2\bar{H}_{H_2} - \bar{H}_{CH_4} = -\Delta H^{\circ}_{f,CH_4}$$
$$\Delta H_{II} = \bar{H}_{O_2} - \bar{H}_{O_2} = 0$$
$$\Delta H_{III} = \bar{H}_{CO_2} - \bar{H}_{C} - \bar{H}_{O_2} = \Delta H^{\circ}_{f,CO_2}$$
$$\Delta H_{IV} = 2\bar{H}_{H_2O} - 2\bar{H}_{H_2} - \bar{H}_{O_2} = 2\Delta H^{\circ}_{f,H_2O}$$

$$\therefore \quad \Delta H_{rx} = 2\Delta H^{\circ}_{f,H_2O} + \Delta H^{\circ}_{f,CO_2} - \Delta H^{\circ}_{f,CH_4}$$

In general,

$$\Delta H_{rx} = \sum_i \nu_i \Delta H^{\circ}_{f,i}\,(\text{products}) - \sum_i \nu_i \Delta H^{\circ}_{f,i}\,(\text{reactants})$$

$\nu \equiv$ stoichiometric coefficient

- ΔH at constant p and for reversible process is $\Delta H = q_p$

$\Rightarrow$ The heat of reaction is the heat flowing into the reaction from the surroundings

If $\Delta H_{rx} < 0$, $q_p < 0$ heat flows from the reaction to the surroundings (exothermic)

If $\Delta H_{rx} > 0$, $q_p > 0$ heat flows into the reaction from the surroundings (endothermic)

EX /

$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$

Sol /

$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$

$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$

$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$

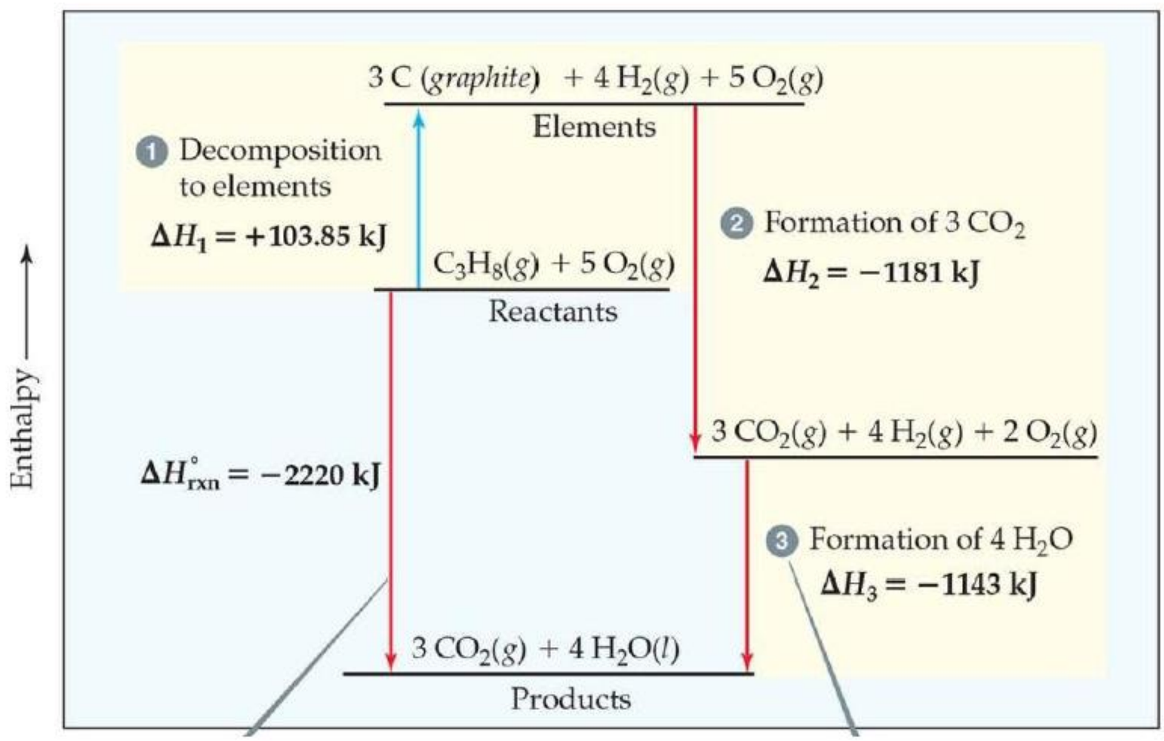
$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$

ΔH_{rxn}^{0} = [(3 mol)(-393.5 kJ/mol) + (4 mol)(-285.8 kJ/mol)] - [(1 mol)(-103.85 kJ/mol) + (5 mol)(0 kJ)]

= [(-1180.5 kJ) + (-1143.2 kJ)] - [(-103.85 kJ) + (0 kJ)]

= (-2323.7 kJ) - (-103.85 kJ)

= -2219.9 kJ



Temperature dependence of ΔH_{rx}

Recall $$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

$$\therefore \quad \left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p = \sum_i \nu_i C_{p,i}\,(\text{products}) - \sum_i \nu_i C_{p,i}\,(\text{reactants})$$

e.g.

CH_4 (g, T,1 bar) + $2O_2$ (g, T,1 bar) = CO_2 (g, T,1 bar) + $2H_2O$(l, T, 1 bar)

$$\Delta C_p = \bar{C}_{p,CO_2}(\text{g},\ T, 1\ \text{bar}) + 2\bar{C}_{p,H_2O}(l,\ T, 1\ \text{bar}) - \bar{C}_{p,CH_4}(\text{g},\ T, 1\ \text{bar}) - 2\bar{C}_{p,O_2}(\text{g},\ T, 1\ \text{bar})$$

$$\int_{T_1}^{T_2} \underbrace{\left(\frac{\partial \Delta H}{\partial T}\right)_p}_{\Delta C_p} dT = \Delta H(T_2) - \Delta H(T_1)$$

$$\boxed{\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT}$$

Especially simple when ΔC_p is T-independent