Thermochemistry

• **Goal:** To predict $\Delta H$ for every reaction, even if it cannot be carried out in the laboratory

The heat of reaction $\Delta H_{rx}$ is the $\Delta H$ for the isothermal reaction at constant pressure.

e.g. $\text{Fe}_2\text{O}_3(s, T, p) + 3\text{H}_2(g, T, p) = 2\text{Fe}(s, T, p) + 3\text{H}_2\text{O}(l, T, p)$

$$\Delta H_{rx}(T, p) = 2\bar{H}_{\text{Fe}}(T, p) + 3\bar{H}_{\text{H}_2\text{O}}(T, p) - 3\bar{H}_{\text{H}_2}(T, p) - \bar{H}_{\text{Fe}_2\text{O}_3}(T, p)$$

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

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

• Define a reference scale for 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

\[
\begin{align*}
\bar{H}_{\text{H}_2(\text{g})}^{\circ}(298.15\text{K}) &= 0 \\
\bar{H}_{\text{C(\text{graphite})}}^{\circ}(298.15\text{K}) &= 0
\end{align*}
\]

The "$^{\circ}$" means 1 bar

• $H_f^{\circ}(298.15\text{K})$: We can now write reactions to form 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.
Example (let $T = 298.15 \, \text{K}$)

\[
\frac{1}{2} \, \text{H}_2 (g, T, 1 \, \text{bar}) + \frac{1}{2} \, \text{Br}_2 (l, T, 1 \, \text{bar}) = \text{HBr} (g, T, 1 \, \text{bar})
\]

\[
\Delta H_{rx} = \Delta \tilde{H}_f^o (T) = \tilde{H}_{\text{HBr}}^o (g, T) - \frac{1}{2} \tilde{H}_{\text{H}_2}^o (g, T) - \frac{1}{2} \tilde{H}_{\text{Br}_2}^o (l, T)
\]

\[
\therefore \Delta H_f^o (T) = \tilde{H}_{\text{HBr}}^o (g, T)
\]

We can now tabulate $H_f^o (298.15 \, \text{K})$ values for all known compounds.

We can calculate $\tilde{H}_{\text{HBr}}^o (T)$ for any reaction ($T = 298.15 \, \text{K}$).

e.g.

\[
\text{CH}_4 (g, T, 1 \, \text{bar}) + 2 \text{O}_2 (g, T, 1 \, \text{bar}) = \text{CO}_2 (g, T, 1 \, \text{bar}) + 2 \text{H}_2 \text{O}(l, T, 1 \, \text{bar})
\]

- 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 $\Delta H$'s around paths.]

\[
\begin{align*}
\text{CH}_4 (g, T, 1 \, \text{bar}) &= \text{C}_{\text{graphite}} (s, T, 1 \, \text{bar}) + 2 \text{H}_2(g, T, p) & \Delta H_I \\
2 \text{O}_2 (g, T, 1 \, \text{bar}) &= 2 \text{O}_2 (g, T, 1 \, \text{bar}) & \Delta H_{II} \\
\text{C}_{\text{graphite}} (s, T, 1 \, \text{bar}) + \text{O}_2 (g, T, 1 \, \text{bar}) &= \text{CO}_2 (g, T, 1 \, \text{bar}) & \Delta H_{III} \\
2 \text{H}_2(g, T, p) + \text{O}_2 (g, T, 1 \, \text{bar}) &= 2 \text{H}_2 \text{O}(l, T, 1 \, \text{bar}) & \Delta H_{IV}
\end{align*}
\]

\[
\text{CH}_4 (g, T, 1 \, \text{bar}) + 2 \text{O}_2 (g, T, 1 \, \text{bar}) = \text{CO}_2 (g, T, 1 \, \text{bar}) + 2 \text{H}_2 \text{O}(l, T, 1 \, \text{bar})
\]
\[ \Delta H_{\text{rx}} = \Delta H_I + \Delta H_{\text{II}} + \Delta H_{\text{III}} + \Delta H_{\text{IV}} \]

\[ \Delta H_I = \Delta H_{\text{CH}_4} + 2\Delta H_{\text{H}_2} - \Delta H_{\text{CH}_4} = -\Delta H_{\text{f,CH}_4} \]

\[ \Delta H_{\text{II}} = \Delta H_{\text{O}_2} - \Delta H_{\text{O}_2} = 0 \]

\[ \Delta H_{\text{III}} = \Delta H_{\text{CO}_2} - \Delta H_{\text{C}} - \Delta H_{\text{O}_2} = \Delta H_{\text{f,CO}_2} \]

\[ \Delta H_{\text{IV}} = 2\Delta H_{\text{H}_2O} - 2\Delta H_{\text{H}_2} - \Delta H_{\text{O}_2} = 2\Delta H_{\text{f,H}_2O} \]

\[ \therefore \quad \Delta H_{\text{rx}} = 2\Delta H_{\text{f,H}_2O} + \Delta H_{\text{f,CO}_2} - \Delta H_{\text{f,CH}_4} \]

In general,

\[ \Delta H_{\text{rx}} = \sum v_i \Delta H_{f,i}^\circ \text{(products)} - \sum v_i \Delta H_{f,i}^\circ \text{(reactants)} \]

\[ v \equiv \text{stoichiometric coefficient} \]

• \( \Delta H \) at constant \( p \) and for reversible process is \( \Delta H = q_p \)

⇒ The heat of reaction is the heat flowing into the reaction from the surroundings

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

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

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

\[\therefore \left( \frac{\partial \Delta H}{\partial T} \right)_p = \Delta C_p = \sum_{i} v_i C_{p,i} \text{(products)} - \sum_{i} v_i C_{p,i} \text{(reactants)}\]

e.g. \[
\text{CH}_4 \ (g, T, 1 \text{ bar}) + 2\text{O}_2 \ (g, T, 1 \text{ bar}) = \text{CO}_2 \ (g, T, 1 \text{ bar}) + 2\text{H}_2\text{O}(l, T, 1 \text{ bar})
\]

$\Delta C_p = \tilde{C}_{p,\text{CO}_2} \ (g, T, 1 \text{ bar}) + 2\tilde{C}_{p,\text{H}_2\text{O}} \ (l, T, 1 \text{ bar}) - \tilde{C}_{p,\text{CH}_4} \ (g, T, 1 \text{ bar}) - 2\tilde{C}_{p,\text{O}_2} \ (g, T, 1 \text{ bar})$

\[
\int_{T_1}^{T_2} \left( \frac{\partial \Delta H}{\partial T} \right)_p \ dT = \Delta H(T_2) - \Delta H(T_1)
\]

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

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