Statistical Molecular Thermodynamics

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Video 5.9

Thermochemistry
Heat of Reaction

Heat may be absorbed or evolved in a chemical reaction. When that occurs at constant pressure $\Delta H = q_P$ and we define:

$$\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$$

(endo=in)

**Endothermic**

$$q_P = \Delta_r H > 0$$

Absorbs energy as heat, ‘uphill’. Heat must be supplied to drive the reaction.

(exo=out)

**Exothermic**

$$q_P = \Delta_r H < 0$$

Releases (evolves) energy as heat, ‘downhill’. Heat is produced.
**Thermochemistry Examples**

*Exothermic*: combustion of methane,

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

\[ \Delta_r H = -890.36 \text{ kJ at 298 K} \]  
(heat is evolved)

(also referred to as a “heat of combustion” when \( \text{O}_2 \) is a reactant)

*Endothermic*: water-gas reaction,

\[ \text{C(s)} + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) \]

\[ \Delta_r H = 131 \text{ kJ at 298 K} \]  
(heat is required to drive the reaction)
**Enthalpy Is Additive**

$\Delta H$ is a state function, which means it is an additive property

Given $\Delta_r H$ values for (1) and (2)

(1) \( C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta_r H(1) = -110.5 \text{ kJ} \)

(2) \( CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta_r H(2) = -283.0 \text{ kJ} \)

Summation provides $\Delta_r H$ for (3)

(3) \( C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H(3) = (-110.5 \text{ kJ}) + (-283.0 \text{ kJ}) = -393.5 \text{ kJ} \)
**Hess’ Law**

The additivity of $\Delta_r H$ is known as *Hess’ Law*

Another example:

**given**

1. $2\text{P(s)} + 3\text{Cl}_2(\text{g}) \longrightarrow 2\text{PCl}_3(\text{l})$ \hspace{1cm} $\Delta_r H(1) = -640 \text{ kJ}$
2. $2\text{P(s)} + 5\text{Cl}_2(\text{g}) \longrightarrow 2\text{PCl}_5(\text{s})$ \hspace{1cm} $\Delta_r H(2) = -887 \text{ kJ}$

**calculate**

3. $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow \text{PCl}_5(\text{s})$ \hspace{1cm} $\Delta_r H(3) = ?$

Reverse (1), add (2), divide sum by 2:

1. $2\text{PCl}_3(\text{l}) \longrightarrow 2\text{P(s)} + 3\text{Cl}_2(\text{g})$ \hspace{1cm} $\Delta_r H(-1) = 640 \text{ kJ}$
2. $2\text{P(s)} + 5\text{Cl}_2(\text{g}) \longrightarrow 2\text{PCl}_5(\text{s})$ \hspace{1cm} $\Delta_r H(2) = -887 \text{ kJ}$

\[
\frac{2\text{PCl}_3(\text{l}) + 2\text{Cl}_2(\text{g}) \longrightarrow 2\text{PCl}_5(\text{s})}{\div 2} \hspace{1cm} \Delta_r H(-1 + 2) = -247 \text{ kJ}
\]

3. $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow \text{PCl}_5(\text{s})$ \hspace{1cm} $\Delta_r H(3) = -124 \text{ kJ}$