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:

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

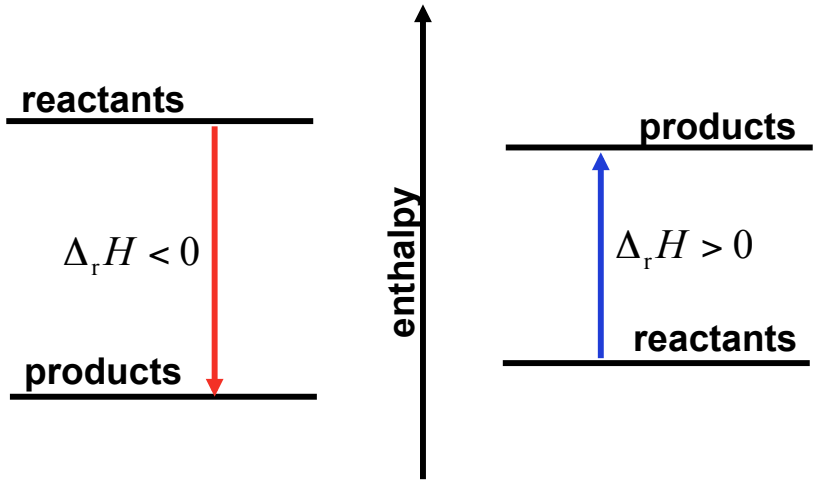
(reaction)

(*exo*=out)

exothermic

$q_P = \Delta_r H < 0$

Releases (evolves) energy as heat, 'downhill'. Heat is produced.



(*endo*=in)

endothermic

$q_P = \Delta_r H > 0$

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

Thermochemistry Examples

***Exo*thermic:** combustion of methane,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

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

(also referred to as a "heat of combustion" when O_2 is a reactant)

***Endo*thermic:** water-gas reaction,

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

$\Delta_r H = 131\ \text{kJ}$ at 298 K (heat is required to drive the reaction)

Enthalpy Is Additive

ΔH is a state function, which means it is an additive property

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

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

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

Summation provides $\Delta_r H$ for (3)

$$(3)\ C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$\Delta_r H(3) = (-110.5\ \text{kJ}) + (-283.0\ \text{kJ}) = -393.5\ \text{kJ}$$

Hess' Law

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

Another example:

given (1) $2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l)$ $\Delta_r H(1) = -640$ kJ

(2) $2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(s)$ $\Delta_r H(2) = -887$ kJ

calculate (3) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$ $\Delta_r H(3) = ?$

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

(–1) $2PCl_3(l) \longrightarrow 2P(s) + 3Cl_2(g)$ $\Delta_r H(-1) = 640$ kJ

(2) $2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(s)$ $\Delta_r H(2) = -887$ kJ

$2PCl_3(l) + 2Cl_2(g) \longrightarrow 2PCl_5(s)$ $\Delta_r H(-1+2) = -247$ kJ

÷2

(3) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$ $\Delta_r H(3) = -124$ kJ