5.60 Thermodynamics & Kinetics
Spring 2008

Thermochemistry

- 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.

- Define a reference scale for enthalpy

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

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

- $\Delta H_f^\circ(298.15K)$: 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 K)

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

$$\Delta H_{rx} = \Delta \bar{H}_f^\circ(\text{products}) - \Delta \bar{H}_f^\circ(\text{reactants})$$

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

We can tabulate $\Delta H_f^\circ(298.15K)$ values for all known compounds.

We can calculate $\Delta \bar{H}_{rx}^\circ(T)$ 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)

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

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

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

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

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

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