Thermochemistry

Much of thermochemistry is based on finding "easy" paths to calculate changes in enthalpy, i.e. understanding how to work with thermodynamic cycles.

- 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 (the complete transfer from reactants to products, not to some equilibrium state).

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 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

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

- $\Delta H_f^\circ(298.15K)$: The heat of formation is the heat of reaction to create 1 mole of that compound from its constituent elements in their most stable forms.

    Example (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)

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

We can tabulate $\Delta H_f^\circ(298.15K)$ values for all known compounds.
We can calculate $\Delta H_{rx}^\circ(298.15K)$ for any reaction.

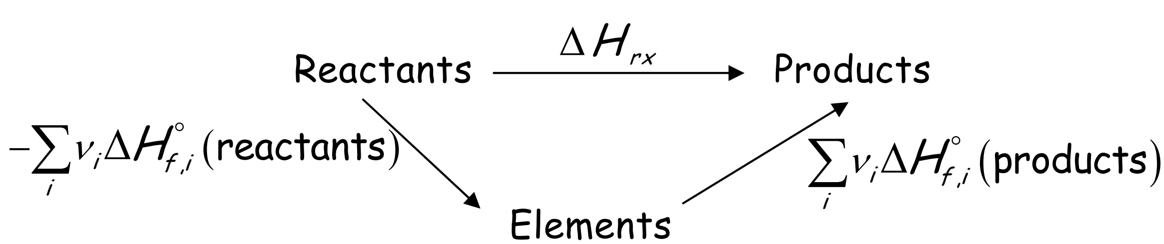
e.g. (T=298.15K)

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 [An example of a thermodynamic cycle applied to thermochemistry]



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)

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

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

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

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 pV 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 <u>to</u> the surroundings (<u>exothermic</u>)

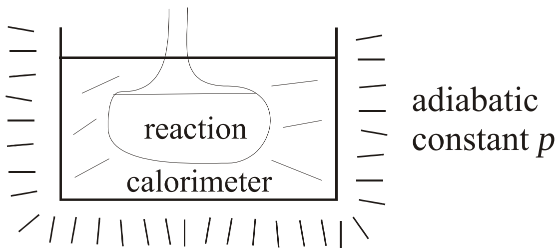
If $\Delta H_{rx} > 0$, $q_p > 0$ heat flows <u>into</u> the reaction from the surroundings (<u>endothermic</u>)

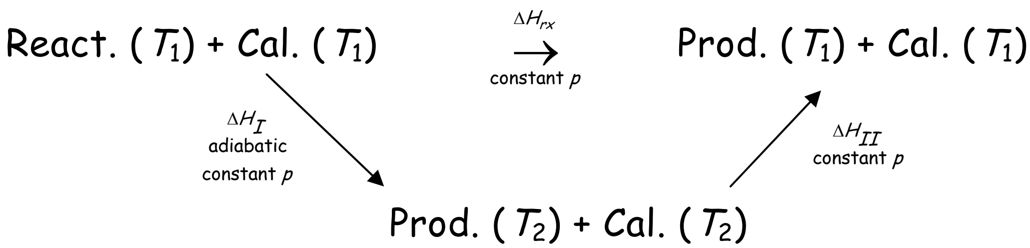
Calorimetry

The objective is to measure

$\Delta H_{rx}(T_1)$ Reactants (T_1) $\underset{\text{constant } p}{\overset{\text{isothermal}}{=}}$ Products (T_1)

- Constant pressure (for solutions)





I) ΔH_I React. (T_1) + Cal. (T_1) $\underset{\text{constant } p}{\overset{\text{adiabatic}}{=}}$ Prod. (T_2) + Cal. (T_2)

II) ΔH_{II} Prod. (T_2) + Cal. (T_2) $\underset{\text{constant } p}{=}$ Prod. (T_1) + Cal. (T_1)

$\Delta H_{rx}(T_1)$ React. (T_1) + Cal. (T_1) $\underset{\text{constant } p}{=}$ Prod. (T_1) + Cal. (T_1)

$$\Delta H_{rx}(T_1) = \Delta H_I + \Delta H_{II}$$

(I) Purpose is to measure (T_2 - T_1)

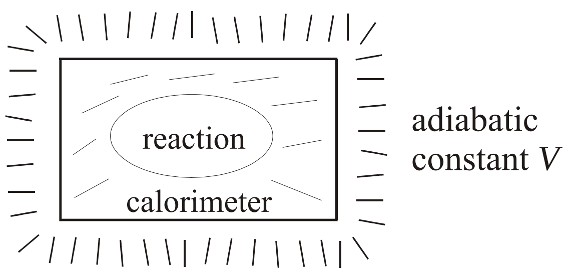
Adiabatic, const. p $\Rightarrow$ $q_p = 0$ $\Rightarrow$ $\Delta H_I = 0$

(II) Purpose is to measure heat q_p needed to take prod. + cal. from T_2 back to T_1.

$$q_p = \int_{T_2}^{T_1} C_p(\text{Prod.} + \text{Cal.})dT = \Delta H_{II}$$

$$\therefore \quad \boxed{\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_p(\text{Prod.} + \text{Cal.})dT}$$

- <u>Constant volume</u> (when gases involved)



React. (T_1) + Cal. (T_1) $\xrightarrow[\text{constant V}]{\Delta U_{rx}}$ Prod. (T_1) + Cal. (T_1)

ΔU_I adiabatic constant V ↘ Prod. (T_2) + Cal. (T_2) ↗ ΔU_{II} constant V

I) ΔU_I React. (T_1) + Cal. (T_1) $\underset{\text{constant } V}{\overset{\text{adiabatic}}{=}}$ Prod. (T_2) + Cal. (T_2)

II) ΔU_{II} Prod. (T_2) + Cal. (T_2) $\underset{\text{constant } V}{=}$ Prod. (T_1) + Cal. (T_1)

$\Delta U_{rx}(T_1)$ React. (T_1) + Cal. (T_1) $\underset{\text{constant } V}{=}$ Prod. (T_1) + Cal. (T_1)

$$\Delta U_{rx}(T_1) = \Delta U_I + \Delta U_{II}$$

(I) Purpose is to measure (T_2 - T_1)

Adiabatic, const. V $\Rightarrow$ $q_V = 0$ $\Rightarrow$ $\Delta U_I = 0$

(II) Purpose is to measure heat q_V needed to take prod. + cal. from T_2 back to T_1.

$$q_V = \int_{T_2}^{T_1} C_V(\text{Prod.} + \text{Cal.})\,dT = \Delta U_{II}$$

$$\therefore \quad \boxed{\Delta U_{rx}(T_1) = -\int_{T_1}^{T_2} C_V(\text{Prod.} + \text{Cal.})\,dT}$$

Now use $H = U + pV$ or $\Delta H = \Delta U + \Delta(pV)$

Assume only significant contribution to $\Delta(pV)$ is from gases.

Ideal gas $\Rightarrow$ $\Delta(pV) = R\Delta(nT)$

Isothermal $T = T_1 \Rightarrow$ $\Delta(pV) = RT_1\Delta n_{gas}$

$$\therefore \quad \begin{array}{|l|}\hline \Delta H_{rx}(T_1) = \Delta U_{rx}(T_1) + RT_1\Delta n_{gas} \\ \\ \Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_V(\text{Prod.} + \text{Cal.})\,dT + RT_1\Delta n_{gas} \\ \hline \end{array}$$

e.g. $4\ HCl(g) + O_2(g) = 2\ H_2O(l) + 2\ Cl_2(g)$

T_1 = 298.15 K

$\Delta U_{rx}(T_1)$ = -195.0 kJ Δn_{gas} = -3 moles

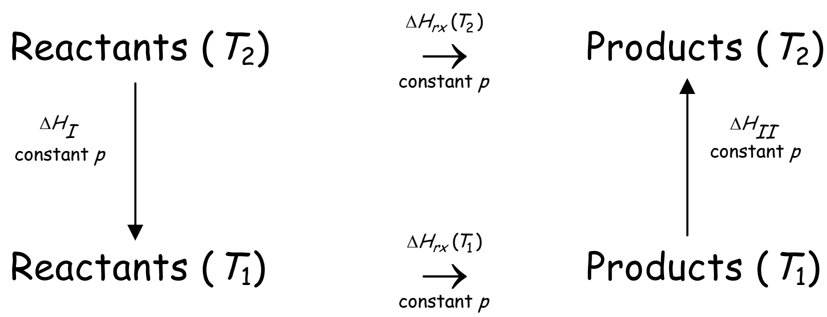
$\Delta H_{rx}(T_1)$ = -195.0 kJ + (-3 mol)(298.15 K)(8.314×10^{-3} kJ/K-mol)

= -202.43 kJ

Temperature dependence of ΔH_{rx}

Suppose know ΔH_{rx} at some temperature T_1 (e.g. at 298.15 K) and we want to know it at some other temperature T_2.

Generally the difference is small… often we assume that there is no temperature dependence if the difference between T_1 and T_2 is "small". If the difference between T_1 and T_2 is large enough, we can calculate $\Delta H_{rx}(T_2)$ from the heat capacities of the reactants and products (assuming no phase change in any component).



$$\Delta H_{rx}(T_2) = \Delta H_I + \Delta H_{rx}(T_1) + \Delta H_{II}$$

$$\Delta H_{rx}(T_2) = \Delta H_{rx}(T_1) + \int_{T_2}^{T_1} C_p(react.)dT + \int_{T_1}^{T_2} C_p(prod.)dT$$

$$\Delta H_{rx}(T_2) = \Delta H_{rx}(T_1) + \int_{T_1}^{T_2} \left[C_p(prod.) - C_p(react.)\right] dT$$

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