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.
$$\left.\begin{aligned} \bar{H}^{\circ}_{H_2(g)}(298.15\text{K}) = 0 \\ \bar{H}^{\circ}_{C\,(\text{graphite})}(298.15\text{K}) = 0 \end{aligned}\right\} \text{ The "}\circ\text{" means 1 bar}$$

- $\Delta H_f^\circ(298.15\text{K})$: 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.

<u>Example</u> (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)

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

We can tabulate $\Delta H_f^\circ(298.15\text{K})$ values for all known compounds.
We can <u>calculate</u> $\Delta H_{rx}^\circ(298.15\text{K})$ 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]

$$\begin{tikzcd}
\text{Reactants} \arrow[rr, "\Delta H_{rx}"] \arrow[dr, "-\sum_i \nu_i \Delta H^\circ_{f,i}(\text{reactants})"'] & & \text{Products} \\
& \text{Elements} \arrow[ur, "\sum_i \nu_i \Delta H^\circ_{f,i}(\text{products})"'] &
\end{tikzcd}$$

$$
\begin{array}{ll}
CH_4\ (g,T,1\ \text{bar}) = C_{graphite}\ (s,T,1\ \text{bar}) + 2H_2(g,T,p) & \Delta H_{I} \\
2O_2\ (g,T,1\ \text{bar}) = 2O_2\ (g,T,1\ \text{bar}) & \Delta H_{II} \\
C_{graphite}\ (s,T,1\ \text{bar}) + O_2\ (g,T,1\ \text{bar}) = CO_2\ (g,T,1\ \text{bar}) & \Delta H_{III} \\
2H_2(g,T,p) + O_2\ (g,T,1\ \text{bar}) = 2H_2O(l,T,\ 1\ \text{bar}) & \Delta H_{IV}
\end{array}
$$

$$CH_4\ (g,T,1\ \text{bar}) + 2O_2\ (g,T,1\ \text{bar}) = CO_2\ (g,T,1\ \text{bar}) + 2H_2O(l,T,\ 1\ \text{bar})$$

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

$$\Delta H_{I} = \bar{H}_C + 2\bar{H}_{H_2} - \bar{H}_{CH_4} = -\Delta H^{\circ}_{f,CH_4}$$

$$\Delta H_{II} = \bar{H}_{O_2} - \bar{H}_{O_2} = 0$$

$$\Delta H_{III} = \bar{H}_{CO_2} - \bar{H}_C - \bar{H}_{O_2} = \Delta H^{\circ}_{f,CO_2}$$

$$\Delta H_{IV} = 2\bar{H}_{H_2O} - 2\bar{H}_{H_2} - \bar{H}_{O_2} = 2\Delta H^{\circ}_{f,H_2O}$$

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

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 $\Delta H = q_p$

⇒ 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 from the reaction <u>to</u> the surroundings (<u>exothermic</u>)

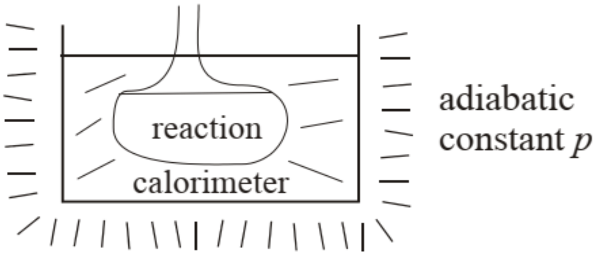
If $\Delta H_{rx} > 0, \quad q_p > 0$ heat flows <u>into</u> the reaction from the surroundings (<u>endothermic</u>)

Calorimetry

The objective is to measure

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

- Constant pressure (for solutions)



$$\begin{tikzcd}
\text{React. } (T_1) + \text{Cal. } (T_1) \arrow[rr, "\Delta H_{rx}", "\text{constant } p"'] \arrow[dr, "\Delta H_{I}\ \text{adiabatic}\ \text{constant } p"'] & & \text{Prod. } (T_1) + \text{Cal. } (T_1) \\
& \text{Prod. } (T_2) + \text{Cal. } (T_2) \arrow[ur, "\Delta H_{II}\ \text{constant } p"'] &
\end{tikzcd}$$

$$\begin{array}{lll}
\text{I)} & \Delta H_{I} & \text{React. } (T_1) + \text{Cal. } (T_1) \underset{\text{constant } p}{\overset{\text{adiabatic}}{=}} \text{Prod. } (T_2) + \text{Cal. } (T_2) \\
\text{II)} & \Delta H_{II} & \text{Prod. } (T_2) + \text{Cal. } (T_2) \underset{\text{constant } p}{=} \text{Prod. } (T_1) + \text{Cal. } (T_1) \\
\hline
 & \Delta H_{rx}(T_1) & \text{React. } (T_1) + \text{Cal. } (T_1) \underset{\text{constant } p}{=} \text{Prod. } (T_1) + \text{Cal. } (T_1)
\end{array}$$

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

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

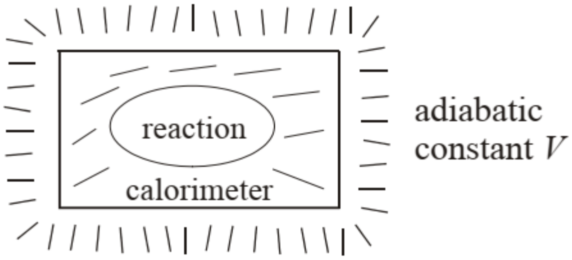
Adiabatic, const. p $\Rightarrow \quad q_p = 0 \quad \Rightarrow \quad \Delta H_I = 0$

(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)



$$\begin{tikzcd}
\text{React. } (T_1) + \text{Cal. } (T_1) \arrow[rr, "\Delta U_{rx}", "\text{constant V}"'] \arrow[dr, "\Delta U_I \text{ adiabatic constant V}"'] & & \text{Prod. } (T_1) + \text{Cal. } (T_1) \\
& \text{Prod. } (T_2) + \text{Cal. } (T_2) \arrow[ur, "\Delta U_{II} \text{ constant V}"'] &
\end{tikzcd}$$

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

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

$\Delta U_{rx}(T_1)$ $\quad$ 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 $\Rightarrow \quad q_V = 0 \quad \Rightarrow \quad \Delta U_{I} = 0$

(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 $\Rightarrow \quad \Delta(pV) = R\Delta(nT)$

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

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

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)($8.314\text{x}10^{-3}$ 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).

$$\begin{tikzcd}
\text{Reactants } (T_2) \arrow[r, "\Delta H_{rx}(T_2)", "\text{constant p}"'] \arrow[d, "\substack{\Delta H_{I} \\ \text{constant p}}"'] & \text{Products } (T_2) \\
\text{Reactants } (T_1) \arrow[r, "\Delta H_{rx}(T_1)", "\text{constant p}"'] & \text{Products } (T_1) \arrow[u, "\substack{\Delta H_{II} \\ \text{constant p}}"']
\end{tikzcd}$$

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

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

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

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