Chemical reactions are always accompanied with a change in energy. It takes energy to make or break chemical bonds.

**Expressions of Energy**

\[ U(T, V) \at \text{Const. } V \quad \Delta U = q_V \]

\[ H(T, P) \at \text{Const. } P \quad \Delta H = q_P \]

**Interconversion between \( \Delta U \) and \( \Delta H \)**

\[ \Delta H_{\text{rxn}} = \Delta U_{\text{rxn}} + (\Delta n_{\text{gas}}) RT \]

Assume:
- \( \Delta (PV) \) is neglected for solids and liquids
- Gases are ideal

Then \( \Delta n_{\text{gas}} = n_{\text{p}} \text{ (products)} - n_{\text{r}} \text{ (reactants)} \)

**Example:**

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \text{ at } 298K \text{ (assume ideal gas)} \]

\[ \Delta H_{298}^\circ - \Delta U_{298}^\circ = \Delta n_{\text{gas}} RT \]

\[ \Delta n_{\text{gas}} = 1 - 1 - \frac{1}{2} = -\frac{1}{2} \quad \text{answer is negative} \]
For a rxn to be...

[Chemical Structures]

endothemic \[ \Delta h > 0 \]

exothermic \[ \Delta h < 0 \]

Consider a general Rxn

\[ n_a A + n_b B + \ldots \rightarrow v_x X + v_y Y + \ldots \]

\[ \Delta_r f^\circ = \sum_i v_i \Delta f^\circ_{i, Produkte} - \sum_i v_i \Delta f^\circ_{i, Reaktionen} \]

Example: Find the expression for the enthalpy change of the following rxn:

\[ \text{CaCO}_3(s) \xrightarrow{\Delta} \text{CaO}(s) + \text{CO}_2(g) \]

\[ \Delta h_r = \Delta f^\circ_{\text{CaO}(s)} + \Delta f^\circ_{\text{CO}_2(g)} - \Delta f^\circ_{\text{CaCO}_3(s)} \]

\[ \text{HCl}(g) \rightarrow H^+(aq) + Cl^-(aq) \]

\[ \Delta h_r = \Delta f^\circ_{H^+(aq)} + \Delta f^\circ_{Cl^-(aq)} - \Delta f^\circ_{\text{HCl}(g)} \]

Enthalpy of formation

Enthalpy change in which the only reaction product is 1 mol of the species of interest

a) Element \( \rightarrow \) molecule

Standard Reference State (s) implies: gas Partial pressure 1 bar

liquid & Solid Pure substance at 1 bar

Solution in Solution

Temperature is 298.15K
**Hess's Law**

$\Delta H$ is path independent, therefore the enthalpy change for any sequence of reactions that sum to the same overall reaction has the same value.

**Example:** Consider the reaction of graphite to diamond

\[ C(s, \text{graphite}) \rightarrow C(s, \text{diamond}) \]

\[ \Delta H_1 \]

\[ C(s, \text{diamond}) + O_2(g) \rightarrow CO_2(g) \quad \Delta fH_2 \]

\[ \Delta H_1 - \Delta H_2 = \Delta fH \]

**Temperature Effects on Enthalpy**

Suppose we want to carry out a run at a temperature other than 298.15 K. How can we relate $\Delta H^\circ$ to $\Delta H$ at this new temperature?

\[ \Delta H(T_{\text{new}}) = \Delta H^\circ(298.15 K) + \int_{298.15 K}^{T_{\text{new}}} \Delta C_p(T') dT' \]

Where \[ \Delta C_p(T') = \sum_i \Delta C_p(T')_{(\text{products})} - \sum_i \Delta C_p(T')_{(\text{reactants})} \]
Energy and Stability

Molecular Stability is proportional to -(Bond enthalpy)

More Stable \( \Rightarrow \) Lower Molecular Energy \( \Rightarrow \) Higher \( H_b \)

Less Stable \( \Rightarrow \) Higher Molecular Energy \( \Rightarrow \) Lower \( H_b \)

i.e) Not stable \( \Rightarrow \) Weak bond \( \Rightarrow \) Small \( H \) (or \( U \))

Example

Given the average Standard bond enthalpy

of C-C is: \( H_b^\circ (C-C) = 348 \text{ KJ/mol} \)

Determine the following relations for bond enthalpy

Using \( >, < \) or \( = \)

Cyclopropane

\( H_b \leq H_b^\circ (C-C) \)

Ring Strain \( \Rightarrow \) Less Stable

Benzene

\( H_b > H_b^\circ (C-C) \)

Bond Conjugation \( \Rightarrow \) more Stable