Thermochemistry deals with the heat flow into or out of a reaction system. Heat flows depend on the energy stored in chemical bonds formed or broken as the reactants are converted into products (system = reaction).

Reaction performed at a constant volume, the heat that flows to or out of the system is equal to \( \Delta U \), and for a constant pressure reaction heat that flows to or out of the system is equal to \( \Delta H \) for the reaction, respectively.

A significant amount of the internal energy or enthalpy of a molecule is stored (as potential energy) in the form of chemical bonds. As the reactants are transformed to products the energy is released or absorbed as the bonds are made or broken.

Thermochemistry
Chemical Reactions and Heat Flow

The \( \Delta U \) or \( \Delta H \) resulting from chemical reactions appears in the surroundings in the form of a temperature increase or decrease resulting from heat flow and work involved in the form of P-V or non P-V work.

If a reaction results in the flow of heat to the surroundings it is described as exothermic (signed negative) and the flow of heat is from the surrounding to effect a reaction, such a reaction is termed endothermic (signed positive).

For a reaction carried out at with reactants and products at standard state (298.15 K and 1 bar) the \( \Delta H \) is annotated as \( \Delta H^o \), note (°).

It is useful to visualize energy changes with energy/enthalpy diagrams.

\[ \text{Enthalpies of Reactions: } \Delta H_R \]

**Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \]

\( \Delta H^o_R = -x \text{ kJ} \)

<table>
<thead>
<tr>
<th>Enthalpy diagram</th>
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<tbody>
<tr>
<td>( \Delta H^o_R )</td>
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<tr>
<td>( \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) )</td>
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1. A thermochemical equation is a chemical equation that includes the value of \( H \). The \( H \) is associated with the reaction stoichiometry.

\[ 2\text{C}_4\text{H}_{10}(\text{l}) + 121 \text{O}_2(\text{g}) \rightarrow 80 \text{CO}_2(\text{g}) + 82 \text{H}_2\text{O}(\text{l}) \quad H = -40,000 \text{ kJ} \]

and

\[ \text{C}_4\text{H}_{12}(\text{l}) + 60.5 \text{O}_2(\text{g}) \rightarrow 40 \text{CO}_2(\text{g}) + 41 \text{H}_2\text{O}(\text{l}) \quad H = -20,000 \text{ kJ} \]

2. Reversing the reaction changes the sign;

\[ 40 \text{CO}_2(\text{g}) + 41 \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_4\text{H}_{12}(\text{l}) + 60.5 \text{O}_2(\text{g}) \quad H = +20,000 \text{ kJ} \]

3. Note that the physical state of species involved is shown.

\( \Delta H \) or \( \Delta H^o \) conceptually is a difference of enthalpy (in this case) and is the enthalpy difference relating to the end and start of a reaction. Conceptually;

\[ \Delta H^o = H^o_{\text{products}} - H^o_{\text{reactants}} \]

In reality, \( H^o \) is not determinable because there is no absolute zero value for \( H \) or \( U \) or \( G \). What is determinable are \( \Delta H \) or \( \Delta U \) or \( \Delta G \).

An arbitrary zero is defined. The arbitrary zero is for elements at their intrinsic state at standard state. This requires the definition of standard enthalpy of formation for a substance.
The (molar) standard enthalpy of formation or (molar) standard heat of formation of a species is the change of enthalpy from the formation of 1 mole of the species from its constituent elements, where all substances in their standard states.

\[ \Delta H_f^o = \Delta H_f^o, \ \text{products} - \Delta H_f^o, \ \text{reactants} \]

By definition, for any element in its standard state, because the reactants and products are identical:

\[ \Delta H_f^o, \ \text{elements} = H_f^o, \ \text{elements} = 0 \text{ at STP.} \]

In general:

\[ \sum v_i \Delta H_f^o, i \]

The unit less stoichiometric coefficients \( v_i \) are positive for products and negative for reactants.

\[ \Delta H_f^o = \sum v_i \Delta H_f^o, i \]

**Hess’s Law**

The Hess’s law states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps.

The enthalpy of a chemical process is independent of the path taken from the initial to the final state because enthalpy is a state function.

Hess's law is an expression of the principle of conservation of energy, i.e. the first law of thermodynamics.
Definition: **Average bond enthalpy** is the enthalpy change $\Delta H$, when one mole of bonds are broken in a substance at 298.15 K.

Definition: **Average bond energy** is the internal energy change $\Delta U$, when one mole of bonds are broken in a substance at 298.15 K.

\[
\begin{align*}
2 \text{H}_2 + 2 \text{Cl}_2 &\rightarrow 4 \text{HCl} \\
\Delta H = -432 \text{kJ/mol} \\
\Delta H_{\text{H}-\text{Cl}} &= -432 \text{kJ/mol} \\
\Rightarrow \Delta H &= 4 \times \Delta H_{\text{H}-\text{Cl}} \\
\Rightarrow \Delta U &= \Delta H - nRT \\
\Rightarrow \Delta U &= \Delta H - nRT(\Delta n)
\end{align*}
\]

**Example Problem 4.1**

The average bond enthalpy of the O—H bond in water is defined as one-half of the enthalpy change for the reaction $\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + \text{O}_2(g)$. The formation enthalpies, $\Delta H_f$, for $\text{H}_2(g)$ and $\text{O}_2(g)$ are 218.0 and 249.8 kJ/mol, respectively, at 298.15 K, and $\Delta H_f$ for $\text{H}_2\text{O}(g)$ is $-241.8$ kJ/mol at the same temperature.

a. Use this information to determine the average bond enthalpy of the O—H bond in water at 298.15 K.

b. Determine the average bond energy $\Delta U$ of the O—H bond in water at 298.15 K. Assume ideal gas behavior.

\[
\Delta U = \Delta H - nRT = \Delta H - RT(\Delta n)
\]

b. $\Delta U = \Delta H - \Delta PV \\
\Rightarrow \Delta U = \Delta H - \Delta(nRT) = \Delta H - RT(\Delta n)$

\[
\begin{align*}
\Delta H &= \Delta H_f(\text{H}_2) + \Delta H_f(\text{O}_2) - \Delta H_f(\text{H}_2\text{O}) \\
&= 218.0 + 249.8 - (-241.8) \\
&= 419.6 \text{ kJ/mol}
\end{align*}
\]

\[
\begin{align*}
\Delta U &= \Delta H - RT(\Delta n) \\
&= 419.6 - (8.314 \text{ J/mol} \cdot \text{K}^{-1}) \times 298.15 \text{ K} \\
&= 507.3 \text{ kJ/mol}
\end{align*}
\]

The average value for $\Delta H_f$ for the O—H bond in water is $\frac{1}{2} \times 922.0$ kJ/mol$^{-1} = 461.0$ kJ/mol$^{-1}$. The bond energy and the bond enthalpy are nearly identical.

\[
\Delta H_{\text{O—H}} = \frac{1}{2} \times 922.0 \text{ kJ/mol}^{-1}
\]

**Temperature dependence of $\Delta H_f$:**

For a substance: $\Delta H_f^o = \Delta H_{f,298} + \int_{298}^{T} C_p dT$

For a reaction: $\Delta H_f^o = \Delta H_{f,298} + \int C_p dT$

where, $\Delta C_p = \sum C_{p,i}$ may be $T$ dependent.
Determination of $\Delta U$ and $\Delta H$ of reactions, $\Delta n \neq 0$:

$\Delta n =$ change number of gas molecules

$= (\text{#gaseous product moles}) - (\text{#gaseous reactant moles})$

& if we set $\Delta V=0$, $\Delta U = q_v = C_{\text{bomb calorimeter}} \Delta T$

Run a reaction in a constant volume of system, determine $q_v$ and calculate the internal energy change of the reaction, and use the quantitative relationships to calculate enthalpy change for the reaction.

$\Delta U = \Delta H - \Delta (PV) \Rightarrow \Delta U = \Delta H - \Delta (nRT) = \Delta H - RT(\Delta n)$

\[ \Delta U = \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} = \left( \frac{m_{mol}}{M_{mol}} \right) \times C_{\text{prod}}(H_2O) \times \Delta T + C_{\text{calorimeter}} \times \Delta T = 0 \]

Energy balance:

\[ \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} + C_{\text{calorimeter}} \Delta T = 0 \]

Bomb calorimeter

\[ m_{mol} C_{\text{calorimeter}} \Delta T + C_{\text{calorimeter}} \Delta T = \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} \]

\[ \frac{m_{mol}}{M_{mol}} C_{\text{prod}}(H_2O) \Delta T + C_{\text{calorimeter}} \Delta T = 0 \]

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Energy balance: $\frac{m_{mol}}{M_{mol}} C_{\text{prod}}(H_2O) \Delta T + C_{\text{calorimeter}} \Delta T = \frac{m_i}{M_{i}} \Delta U_{\text{combustion}}$

\[ \frac{1812 \times 10^3}{18.02} \times 753.2 \times 0.972 = -0.391 \times 10^5 \]

\[ C_{\text{calorimeter}} = 7.5 \times 10^5 \text{ J/(C)} \]

\[ \Delta U_{\text{combustion}} = -3.26 \times 10^5 \text{ J} \]

\[ \Delta H = \Delta U + RT(\Delta n) = -3.26 \times 10^5 \text{ J} + 8.314 \times 298.15 \times (-1.5)J = -3.26 \times 10^5 \text{ J} \]

Bomb Calorimetry $\Delta n = 0$ - Combustion Reactions: $\Delta U$

Calorimetry: Measuring heat

Mass $m_i$ (molar mass $M_i$) of the substance is burnt completely in $O_2$.

The heat produced $q_v$ is calculated and related to $\Delta U$ and $\Delta H$, using heat capacity of the bomb calorimeter $C_{\text{calorimeter}}$ etc.

Combustion reactions generates oxides of the compound.

$\Delta U =$ Internal energy change per mole of compound combusted

$\Delta H =$ Enthalpy change per mole of compound combusted

\[ \Delta U = \frac{m_{mol}}{M_{mol}} C_{\text{prod}}(H_2O) \Delta T + C_{\text{calorimeter}} \Delta T = \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} \]

\[ \Delta U = \frac{m_{mol}}{M_{mol}} C_{\text{prod}}(H_2O) \Delta T + C_{\text{calorimeter}} \Delta T = \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} \]

Two stage experiment;

i. determine $C_{\text{calorimeter}}$

ii. determine $\Delta U_{\text{combustion}}$

\[ \text{EXAMPLE PROBLEM 2.1} \]

\[ \text{Given } \text{ C}_6\text{H}_6(\text{l}) + 15/2 \text{ O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}); \text{ } \Delta U, \Delta H =? \]

Limiting reagent

Determination of $\Delta U$ and $\Delta H$ of reactions, $\Delta n = 0$:

Reactions in solution with no gases involved.

$\Delta U = \Delta H - P \Delta V$

& $\Delta V$=0, $\Delta U = \Delta H$

$\Delta U = \Delta H = q$

$\Delta n =$ change number of gas molecules = 0

$\frac{m_{mol}}{M_{mol}} C_{\text{prod}}(H_2O) \Delta T + C_{\text{calorimeter}} \Delta T + \frac{m_i}{M_{i}} \Delta U_{\text{combustion}} = 0$