Definition:

Internal Energy:  $U \Rightarrow \text{Sum Total Energy}$

The sum of all of the kinetic and potential energy contributions to the energy of all the atoms, ions, molecules, etc. in the system.
First Law of Thermodynamics: **Conservation of Energy**

\[ \Delta U = q + w \quad \text{For a Closed System} \]

\[ \Delta U = 0 \quad \text{For an Isolated System} \]

The change in internal energy (\( \Delta U \)) of a **closed system** is equal to the sum of the heat (\( q \)) added to it and the work (\( w \)) done upon it, the internal energy of an isolated system is constant.

Internal energy is a **state** function.
- Quantity is independent of path.

Volume, Temperature, Pressure, and quantity are other examples of **state** functions.
First Law of Thermodynamics: (continued)

\[ \Delta U = q + w \]

Closed system
Constant volume

\[ w = -P \Delta V = 0 \]  No work done

Heat energy is stored as internal energy and released as work.

Closed system
Expansion against external pressure

\[ \Delta U = q + w = q - P_{ex} \Delta V \]
It is frequently most convenient to carry out a process at constant pressure.

- Cooking dinner
- Drying the laundry
- Digesting dinner
- Synthesizing a compound in lab

At constant pressure if only PV work is done:

\[ \Delta U = q + w = q_p - \int_{v_1}^{v_2} P \, dV \]
\[ = q_p - P \int_{v_1}^{v_2} dV = q_p - P \Delta V \]

\[ \Delta H = \Delta U + P \Delta V = q_p \]

Enthalpy is the heat transferred in a process at constant pressure (assuming only PV work).
Equilibrium Thermodynamics

- Open System
  Mass, heat, energy flow freely
- Closed System
  Heat, energy flow freely
- Isolated System
  No mass, heat, or energy flow

Exothermic

\[ q < 0 \]
\[ \Delta H < 0 \]

Endothermic

\[ q > 0 \]
\[ \Delta H > 0 \]
Enthalpy and Internal Energy are **State Quantities**: 

∴ We need only be concerned with change in enthalpy ($\Delta H$) or change in internal energy ($\Delta U$) in any process.

Arbitrarily assign $H=0$ for each element in its **Standard State**: Most stable state of aggregation at $P = 1$ atm, $T = 298$ K.

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**Standard Formation Reaction**: Formation of one mole of a substance from the elements in their standard states.

\[
\begin{align*}
\text{CS}_2(\text{l}) & \quad +87.86 \text{ kJ/mol} \\
\text{C}(\text{graphite}) & \quad \text{C}(\text{graphite}) \\
\text{O}_2(\text{g}) & \quad \text{O}_2(\text{g}) \\
\text{S}(\text{s, rhombic}) & \quad \text{S}(\text{s, rhombic}) \\
\text{CO}(\text{g}) & \quad -110.52 \text{ kJ/mol} \\
\text{CO}_2(\text{g}) & \quad -393.51 \text{ kJ/mol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CS}_2(\text{l}) & \quad \rightarrow \quad \text{C}(\text{graphite}) + 2 \text{ S}(\text{s, rhombic}) \\
\text{CO}_2(\text{g}) & \quad \rightarrow \quad \text{C}(\text{graphite}) + \frac{1}{2} \text{ O}_2(\text{g}) \\
\text{CO}_2(\text{g}) & \quad \rightarrow \quad \text{C}(\text{graphite}) + \text{ O}_2(\text{g})
\end{align*}
\]
Hess’s Law: $\Delta H = 0$ for a cyclic process.

$$\Delta H_{AB} + \Delta H_{BC} + \Delta H_{CA} = 0$$

$$\Delta H_R = \sum \Delta H_f^{\ominus (Prod.)} - \sum \Delta H_f^{\ominus (React.)}$$
Heat: Heat always flows from the “hot” object to the “cool” object.

- Initially $T_1 > T_2$
- Heat flow will continue until $T_1 = T_2$

Temperature change ($\Delta T = T_f - T_i$) is proportional to the heat ($q$) received.

$$q \propto \Delta T$$

$$q = C \Delta T$$

Proportionality constant is the heat capacity, $C$.

If heat flows out of the system:

$$\Delta T = T_f - T_i < 0$$

$$q < 0$$

If heat flows into the system:

$$\Delta T = T_f - T_i > 0$$

$$q > 0$$