Thermodynamics: The First Law
Atkins, Chapter 2

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

$q < 0$ Exothermic

$q > 0$ Endothermic
**Internal Energy U**

The sum of all of the kinetic and potential energy contributions to the energy of all the atoms, ions, molecules, etc. in the system.

**Internal Energy U:**

**He gas**
- Translational Energy

**Methanol Gas**
- Rotational Energy
- Vibrational Energy
- Bond Energy
- Nuclear Energy
- Electronic Energy
- Bond Energy

**Nils Walter: Chem 260**
The First Law of Thermodynamics: Internal Energy is Conserved

- 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.

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

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

Internal energy $U$ is a state function $\Rightarrow$ Quantity is independent of path.

Volume, Temperature, Pressure, and Quantity are other examples of state functions.
Internal Energy can be exchanged with the surroundings as heat or work

\[ \Delta U = q + w \]

Closed system, constant volume

Closed system, expansion against external pressure

Heat is stored as internal energy and released as volume-pressure work [J]

\[ \Delta U = q + w = q - p_{ex} \Delta V \]

\( w = -Fdx = -p \Delta V \)

\( w = 0; \text{ no work done} \)

\( \Rightarrow \Delta U = q_v \)
**Internal Energy and Enthalpy**

**Enthalpy definition:**

\[ H = U + pV \]

Most convenient for processes at constant pressure:
- Cooking dinner
- Drying the laundry
- Digesting dinner
- Synthesizing a compound in lab

At constant pressure, if only \( pV \) work is done:

\[
\Delta U = q + w = q_p - \int_{V_1}^{V_2} p \, dV
\]

\[
= q_p - p \int_{V_1}^{V_2} dV = q_p - p(V_2 - V_1) = q_p - p\Delta V
\]

\( p \) independent of \( V \)

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

Enthalpy is the heat transferred in a process at constant pressure (assuming only \( pV \) work)
Enthalpy

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Heating processes:
- **Exothermic**: $\Delta H < 0$
- **Endothermic**: $\Delta H > 0$
Enthalpy and Internal Energy are State Functions

We only need be concerned with the change in enthalpy ($\Delta H$) or change in internal energy ($\Delta U$), not the path of how we got there

$\Rightarrow$ We can arbitrarily assign $H = 0$ for each element in its standard state = state of aggregation at $p = 1$ bar, $T = 298.15$ K

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

- $\Delta_f H =$ standard molar enthalpies of formation

\[
\begin{align*}
\text{CS}_2 (l) & \quad +87.86 \text{ kJ/mol} \\
\text{C}_{(\text{graphite})} + 2 \text{ S}_{(s, \text{rhombic})} & \rightarrow \text{CS}_2(l) \\
\text{C}_{(\text{graphite})} & - \text{C}_{(\text{graphite})} \quad - \quad 0 \\
\text{O}_2 (g) & \quad \text{S}_{(s, \text{rhombic})} \\
\text{CO} (g) & -110.52 \text{ kJ/mol} \\
\text{C}_{(\text{graphite})} + \frac{1}{2} \text{O}_2 (g) & \rightarrow \text{CO} (g) \\
\text{CO}_2 (g) & -393.51 \text{ kJ/mol} \\
\text{C}_{(\text{graphite})} + \text{O}_2 (g) & \rightarrow \text{CO}_2(g)
\end{align*}
\]