Work, Heat, and the First Law

- Work: \( w = F \cdot A \)
  - applied force \( F \) 
  - distance \( A \)

Expansion work

\[ F = p_{\text{ext}}A \]

\[ w = -(p_{\text{ext}}A)A = - p_{\text{ext}} \Delta V \]

**Convention:** Having a "-" sign here implies \( w > 0 \) if \( \Delta V < 0 \), that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings \((\Delta V > 0)\) then \( w < 0 \).

If \( p_{\text{ext}} \) is not constant, then we have to look at infinitesimal changes

\[ d-w = -p_{\text{ext}}dV \]

\( d - \) means this is not an exact differential

**Integral**

\[ w = - \int_{1}^{2} p_{\text{ext}}dV \]  

depends on the path!!!

- Path dependence of \( w \)

**Example:** assume a reversible process so that \( p_{\text{ext}} = p \)

\[ Ar \ (g, p_1, V_1) = Ar \ (g, p_2, V_2) \]

Compression \( V_1 > V_2 \) and \( p_1 < p_2 \)
Two paths:

(1) First \( V_1 \rightarrow V_2 \) at \( p = p_1 \) then \( p_1 \rightarrow p_2 \) at \( V = V_2 \)

(2) First \( p_1 \rightarrow p_2 \) at \( V = V_1 \) then \( V_1 \rightarrow V_2 \) at \( p = p_2 \)

\[
\begin{align*}
\text{Ar}(g, p_1, V_1) &= \text{Ar}(g, p_1, V_2) = \text{Ar}(g, p_2, V_2) \\
\text{Ar}(g, p_1, V_1) &= \text{Ar}(g, p_2, V_1) = \text{Ar}(g, p_2, V_2)
\end{align*}
\]

\[
\begin{align*}
\mathbf{w}_{(1)} &= - \int_{V_1}^{V_2} p \text{ext} \, dV - \int_{V_1}^{V_2} p^{\text{ext}} \, dV \\
&= - \int_{V_1}^{V_2} p \, dV = -p (V_2 - V_1) \\
\mathbf{w}_{(2)} &= - \int_{V_1}^{V_2} p \text{ext} \, dV - \int_{V_1}^{V_2} p^{\text{ext}} \, dV \\
&= - \int_{V_1}^{V_2} p \, dV = -p (V_2 - V_1)
\end{align*}
\]

(Note \( w > 0 \), work done to system to compress it)

\[
\mathbf{w}_{(1)} \neq \mathbf{w}_{(2)} !!!!
\]

Note for the closed cycle [path (1)] - [path (2)],

\( w \) is not a state function

\[ \oint dw \neq 0 \quad \text{closed cycle} \]

cannot write \( w = f(p, V) \)
**Work**

Work ($w$) is not a function of state.

For a cyclic process, it is possible for \[ \int \text{d}w \neq 0 \]

- **Heat**

That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.

Sign convention:
- If heat enters the system, then it is positive.

Heat ($q$), like $w$, is a function of path. Not a state function

It is possible to have a change of state

\[ (p_1, V_1, T_1) = (p_2, V_2, T_2) \]

- adiabatically (without heat transferred)
- nonadiabatically.

Historically measured in calories

\[ 1 \text{ cal} = \text{heat needed to raise } 1 \text{ g } H_2O \text{ } \text{1°C, from } 14.5\text{°C to 15.5°C} \]

The modern unit of heat (and work) is the Joule.

\[ 1 \text{ cal} = 4.184 \text{ J} \]
Heat Capacity

- connects heat with temperature

\[ dq = C_{\text{path}} \, dT \quad \text{or} \quad C_{\text{path}} = \left| \frac{dq}{dT} \right| \]

heat capacity is path dependent

Constant volume: \( C_V \)
Constant volume: \( C_p \)

\[ \therefore \quad q = \int_{\text{path}} C_{\text{path}} dT \]

Equivalence of work and heat

[Joule (1840's)]

Joule showed that it's possible to raise the temperature of \( \text{H}_2\text{O} \)

(a) with only heat

(b) with only work
(weight falls & churns propeller)
Experimentally it was found that

\[ \int (\, dw + dq \,) = 0 \]

\[ \Rightarrow \quad \text{The sum } (w + q) \text{ is independent of path} \]

\[ \Rightarrow \quad \text{This implies that there is a state function whose differential is } \]

\[ dw + dq \]

We define it as \( U \), the "internal energy" or just "energy"

\[ \therefore \quad dU = dw + dq \]

For a cyclic process \( \int dU \neq 0 \)

For a change from state 1 to state 2,

\[ \Delta U = \int_{1}^{2} dU = U_2 - U_1 = q + w \]

each depends on path individually, but not the sum

For fixed \( n \), we just need to know 2 properties, e.g. \((T, V)\), to fully describe the system.

So

\[ U = U(T, V) \]

\( U \) is an extensive function (scales with system size).

\[ U = \frac{U}{n} \]

is molar energy (intensive function)
Mathematical statement:
\[ dU = -dq + dw \]
or
\[ \Delta U = q + w \]
or
\[ - \int d-q = \int d-w \]

Corollary: Conservation of energy

\[ \Delta U_{\text{system}} = q + w \quad \Delta U_{\text{surroundings}} = -q - w \]

\[ \Rightarrow \Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0 \]

Clausius statement of 1st Law:

The energy of the universe is conserved.