\[\Delta W = -P_{\text{ext}} \, dV\]

\[V_m = \frac{V_{\text{total}}}{n}\]

\[V = n \, V_m\]

Reversible: limiting max work equilibrium states
$1 \rightarrow 2 \rightarrow 1$

no change in system + surroundings
no net work
no net heat exchange

$A + B \rightleftharpoons C + D$ equilibrium

$\rho_{ext} = \rho + SP$

$\Delta W = -p_{ext} \, dV$

$\Delta W = -(\rho + SP) \, dV$

$\Delta W = -pdV - SP \, dV$

Reversible: idealization

hard to establish in practice
\[ dU = dQ + dW \]
\[ dU = C_p \text{th}(T) \, dT - P_{\text{ext}} \, dV \]

**constant volume process**
\[ dU = C_p \text{th}(T) \, dT \]

**constant temp**
\[ dU = -P_{\text{ext}} \, dV \]

**Adiabatic**
\[ dU = dW_{\text{reversible}} \]

U state fn. depends on \( T, V \)
\[ U(T, V) \]

**Total Differential of \( U(T, V) \)**
\[ dU(T, V) = \left( \frac{\partial U}{\partial T} \right)_V \, dT + \left( \frac{\partial U}{\partial V} \right)_T \, dV \]

*partial differential*

*hold V*

*Constant while differentiating*
Constant Volume:

\[ dU(T, V) = \left( \frac{\partial H}{\partial T} \right)_V dT \]

\[ dU(T, V) = dq_V - P_{ext} dv \]

const. vol. heat interaction.

\[ dq_V = \left( \frac{\partial H}{\partial T} \right)_V dT \]

\[ dq_v = C_v(T) dT \]

\[ C_v(T) \equiv \left( \frac{\partial H(T, V)}{\partial T} \right)_V \]

At constant volume:

\[ dU(T, V) = dq_v \]

\[ \Delta U(T, V) = q_v \]
Total Differential of $U(T,V)$

$$dU(T,V) = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

$$dU(T,V) = C_v(T) dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

What is this?

**Joule Free Expansion**

![Diagram of gas and vacuum with insulation]

System: Gas

Process: Open stopper, let gas flow into vacuum

Apply 1st law:

$$dU = \oint_P d\Pi + \oint_{\delta V} = 0$$

Constant $U$ process !!!!!
\[ dU(T, v) = C_v(T) \, dT_u + \left( \frac{\partial Y}{\partial V} \right)_T \, dV_u = C \]

\[-C_v(T) \, dT_u = \left( \frac{\partial Y}{\partial V} \right)_T \, dV_u \]

\[-C_v(T) \, \frac{dT_u}{dV_u} = \left( \frac{\partial Y}{\partial V} \right)_T \]

\[-C_v(T) \, \left( \frac{dT}{dV} \right)_u = \left( \frac{\partial Y}{\partial V} \right)_T \]

\[ \text{Vary } \Delta V \text{ limit } \frac{\Delta T}{\Delta V} \xrightarrow{\Delta V \to 0} \frac{\partial Y}{\partial V} \Delta T \]