

$$PV^\gamma = \text{const} \quad \gamma = \frac{5}{2} \quad (\text{for ideal gas})$$

Isothermal process ($T = \text{const}$)

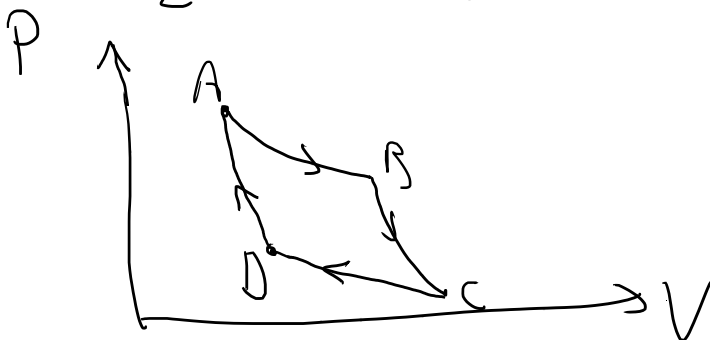
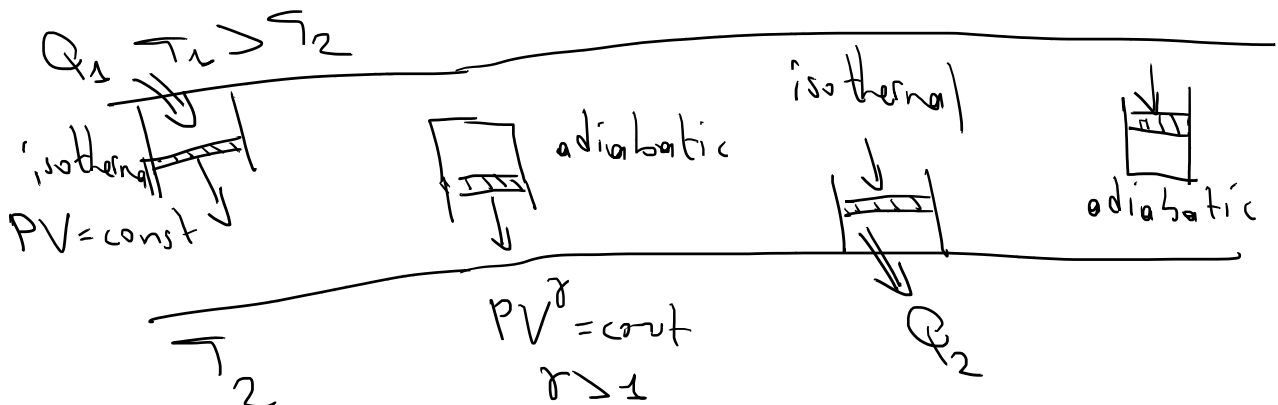
Adiabatic process $\Delta Q = 0 \quad PV^\gamma = \text{const}$

Isothermal process (for the ideal gas)

$$\Delta U = 0$$

$$\Delta Q = \Delta W = NkT \ln\left(\frac{V_f}{V_i}\right)$$

Carnot Cycle



$$\Delta Q_{B \rightarrow C} = 0$$

$$\Delta Q_{D \rightarrow A} = 0$$

$$Q_1 = \Delta Q_{A \rightarrow B} = NkT_1 \ln\left(\frac{V_B}{V_A}\right) > 0$$

$$-Q_2 = \Delta Q_{C \rightarrow D} = -NkT_2 \ln\left(\frac{V_D}{V_C}\right) < 0$$

$$\Delta U = \Delta Q - \Delta W = 0$$

$$\Delta W = \Delta Q = Q_1 - Q_2$$

$$\eta = \frac{\Delta W}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \frac{\ln\left(\frac{V_c}{V_D}\right)}{\ln\left(\frac{V_D}{V_A}\right)}$$

$$PV^\gamma = \text{const} \Rightarrow TV^{\gamma-1} = \text{const}$$

$$\begin{aligned} \Rightarrow \frac{T_1 V_A^{\gamma-1}}{T_1 V_B^{\gamma-1}} &= \frac{T_2 V_D^{\gamma-1}}{T_2 V_C^{\gamma-1}} \Rightarrow \frac{V_A}{V_B} = \frac{V_D}{V_C} \\ \Rightarrow \frac{T_1 V_A^{\gamma-1}}{T_1 V_B^{\gamma-1}} &= \frac{T_2 V_D^{\gamma-1}}{T_2 V_C^{\gamma-1}} \Rightarrow \frac{V_A}{V_B} = \frac{V_D}{V_C} \end{aligned}$$

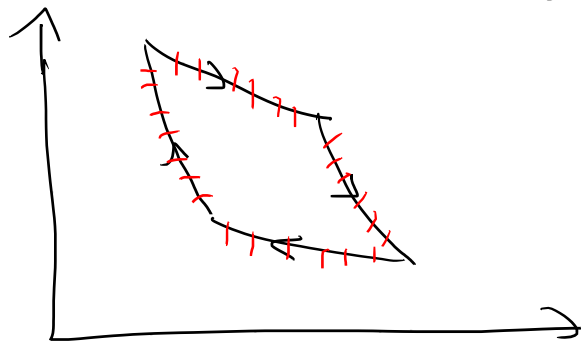
$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \Rightarrow \frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

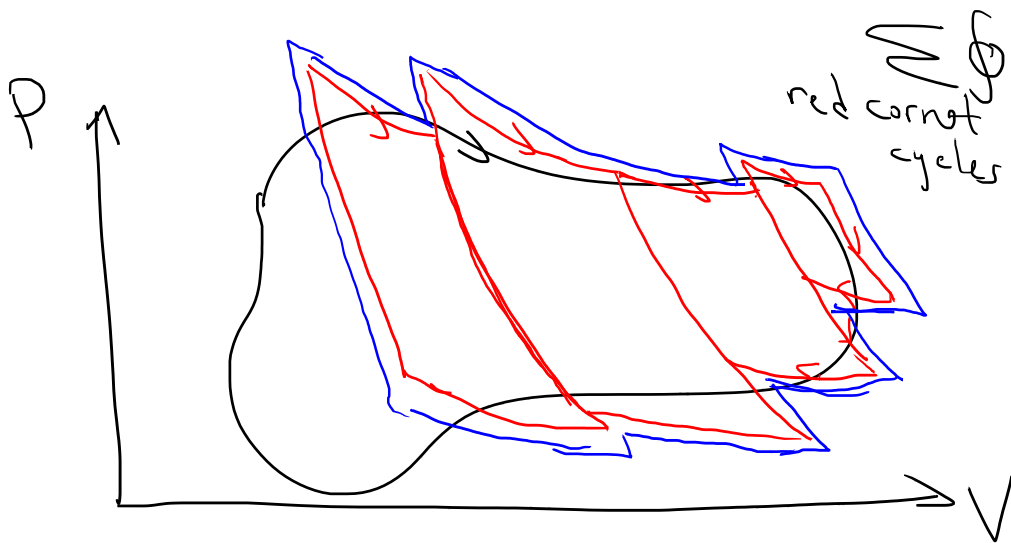
$$\Rightarrow \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0 \Rightarrow \frac{Q_1}{T_1} + \frac{(-Q_2)}{T_2} = 0$$

$$0 = \frac{\Delta Q_{A \rightarrow B}}{T_{A \rightarrow B}} + \frac{\Delta Q_{B \rightarrow C}}{T_{B \rightarrow C}} + \frac{\Delta Q_{C \rightarrow D}}{T_{C \rightarrow D}} + \frac{\Delta Q_{D \rightarrow A}}{T_{D \rightarrow A}}$$

$$= \sum \frac{\Delta Q}{T} = \boxed{\oint \frac{dQ}{T} = 0}$$



$$\oint \frac{dQ}{T} = ?$$



$$\sum \oint \frac{dQ}{T} = \oint \frac{dQ}{T}$$

$\oint \frac{dQ}{T} = 0$ for an arbitrary cycle.

$$\int_A^B \frac{dQ}{T} = S(B) - S(A)$$

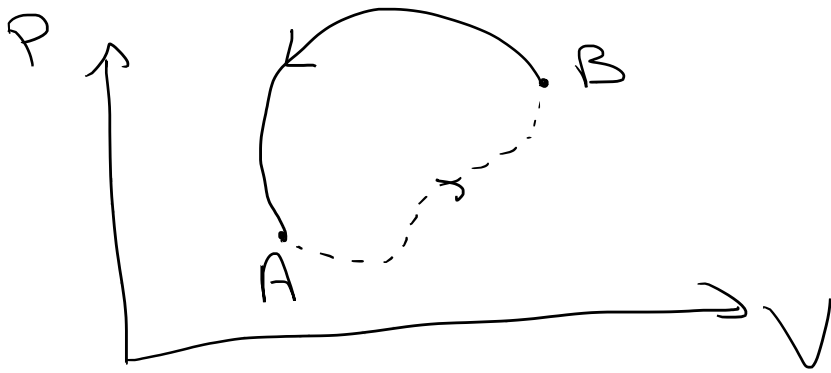
S is the entropy of the system.

$$\boxed{\frac{dQ}{T} = dS}$$

Second Law of Thermodynamics

$$\oint \frac{dQ}{T} \geq 0$$

Corollary in a spontaneously occurring process in an isolated system, entropy either stays the same or increases.



$$\oint \frac{dQ}{T} \geq 0$$

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T} \geq 0$$

non-eq.

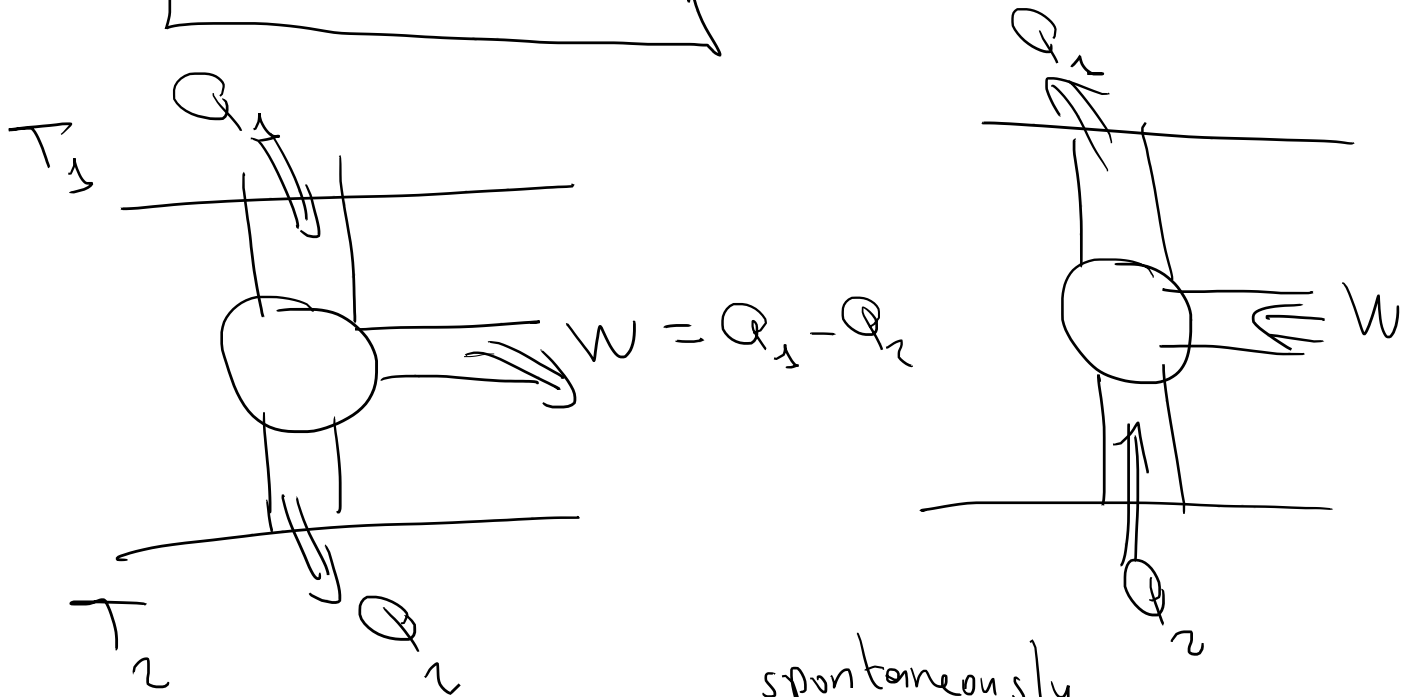
eq.

$$\int_A^B \frac{dQ}{T} + S(A) - S(B) \geq 0$$

$$S(B) \geq S(A) + \int_A^B \frac{dQ}{T}$$

in an isolated system $dQ = 0$

$$\Rightarrow S(B) \geq S(A)$$



Corollary
cold

Heat flow spontaneously from hot to cold



$$\Delta S = \sum \frac{\Delta Q}{T}$$

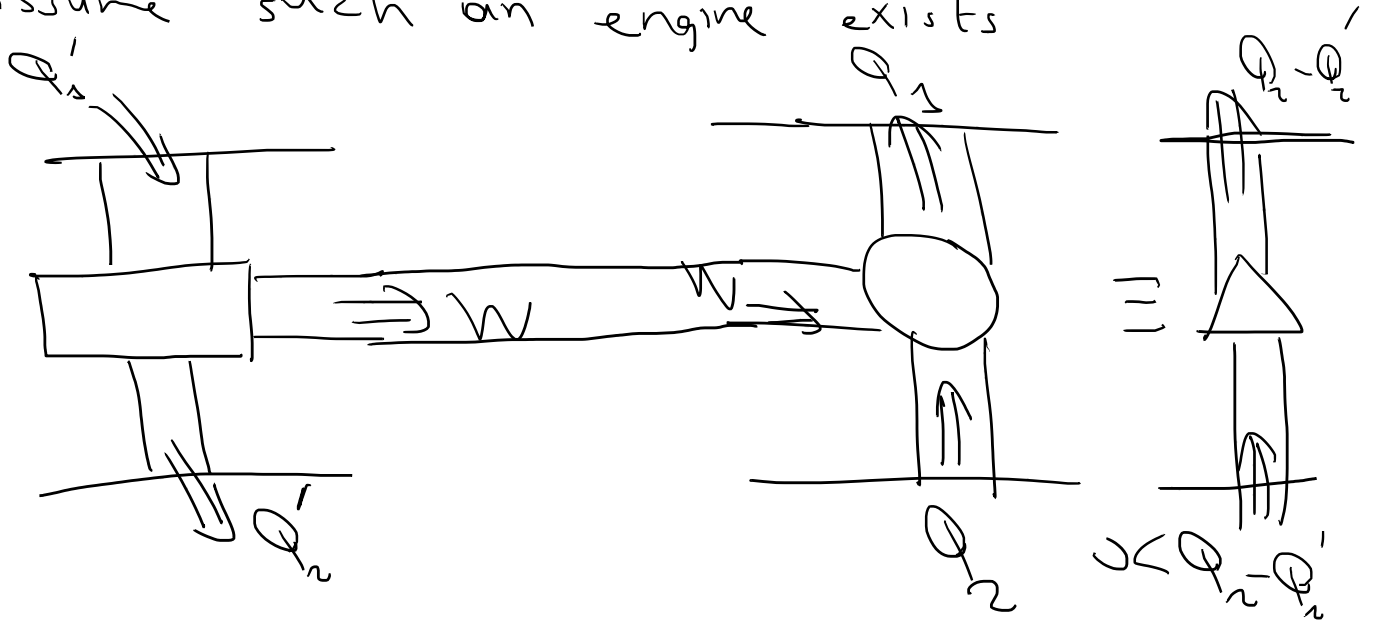
$$= \frac{Q}{T_1} + \frac{-Q}{T_2} \geq 0$$

$$Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \geq 0$$

- i) $T_2 > T_1 \Rightarrow \frac{1}{T_1} < \frac{1}{T_2} \Rightarrow \frac{1}{T_2} - \frac{1}{T_1} > 0 \Rightarrow Q > 0$
- ii) $T_2 < T_1 \Rightarrow \frac{1}{T_2} > \frac{1}{T_1} \Rightarrow \frac{1}{T_2} - \frac{1}{T_1} < 0 \Rightarrow Q < 0$

Corollary No reversible engine can be more efficient than the Carnot engine

Assume such an engine exists



$$\Rightarrow \begin{matrix} Q_1' < Q_1 \\ Q_2' < Q_2 \end{matrix} \Rightarrow \frac{W}{Q_1'} > \frac{W}{Q_1} = \text{contradict the second law}$$

$$W = Q_1' - Q_2' = Q_1 - Q_2$$

$$Q_1' - Q_1 = Q_2' - Q_2 < 0$$

Corollary No reversible engine can be less efficient than the Carnot engine.

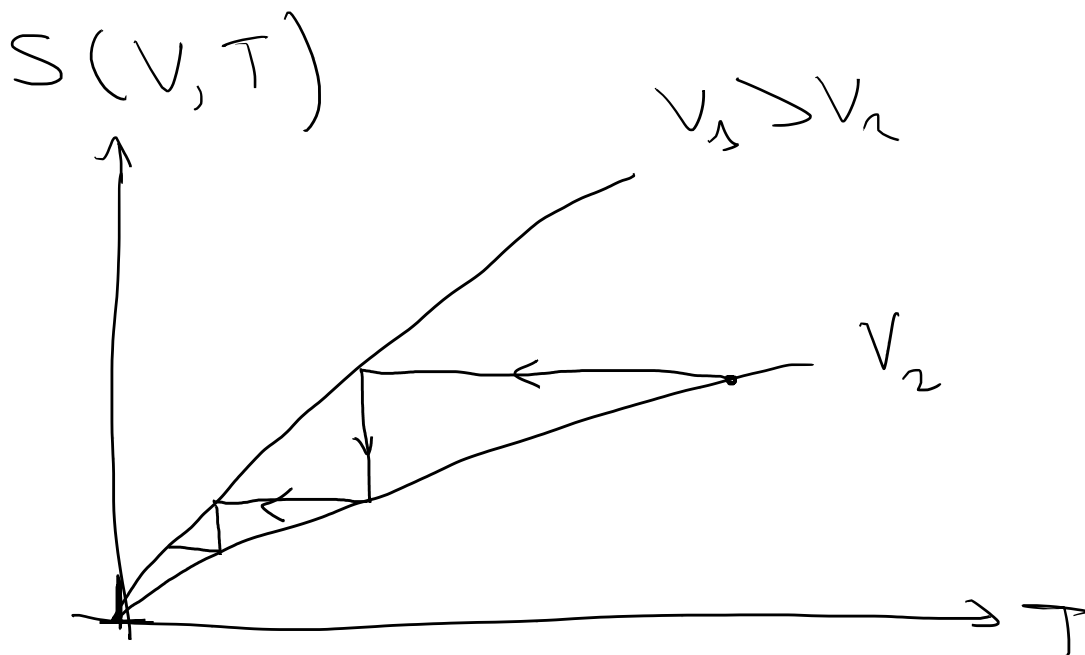
Third Law

$$S(T) \xrightarrow{T \rightarrow 0} 0$$

$\Rightarrow T=0$ can not be reached in a finite amount of time.

macroscopic state of a system $(P, V, T) \quad (E, N)$
 $\uparrow \quad \uparrow$

equation of state : a relation between (P, V, N, T)



$$\Delta U = \Delta Q - \Delta W$$

$$dU = T dS - P dV + \mu dN - \vec{M} \cdot d\vec{B} - \vec{P} \cdot d\vec{E}$$

μ = chemical potential

\vec{E}
 \vec{B} } electric
magnetic } fields.

\vec{M} : magnetization

\vec{P} : polarization of the system

$$dU = T dS - P dV + \mu dN$$

$$T = \left(\frac{\partial U(S, V, N)}{\partial S} \right)_{V, N}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S, N}$$

$$M = \left(\frac{\partial U}{\partial N} \right)_{V, S}$$

$$\left(\frac{\partial T}{\partial N} \right)_{S, V} = \frac{\partial^2 U}{\partial S \partial N} = \frac{\partial^2 U}{\partial N \partial S} = - \left(\frac{\partial P}{\partial N} \right)_{S, V}$$

$$\left(\frac{\partial T}{\partial N} \right)_{S,V} = - \left(\frac{\partial \mu}{\partial S} \right)_{N,V}$$

Maxwell
Relation

$$dU = TdS - PdV + \mu dN$$

$$= d(TS) - SdT - PdV + \mu dN$$

$$d(U - TS) = -SdT - PdV + \mu dN$$

$\underbrace{\hspace{10em}}_{F, \text{ free energy (Helmholtz?)}}$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} \quad \left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{N,V}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$$

$$\mu = + \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

Ex For the ideal gas ($PV = NkT$),
how does energy change with volume?

$$\left(\frac{\partial U}{\partial V} \right)_{T,N} = T \left(\frac{\partial S}{\partial V} \right)_{T,N} - P \left(\frac{\partial V}{\partial V} \right)_{T,N} + \mu \left(\frac{\partial N}{\partial V} \right)_{T,N}$$

$$\left(\frac{\partial U}{\partial V} \right)_{T,N} = T \left(\frac{\partial P}{\partial T} \right)_{N,V} - P \quad \begin{matrix} \parallel \\ 1 \end{matrix} \quad \begin{matrix} \parallel \\ 0 \end{matrix}$$

$$pV = NkT$$

$$p = \frac{Nk}{V} T \Rightarrow \left(\frac{\partial p}{\partial T} \right)_{N,V} = \frac{Nk}{V} = \frac{p}{T}$$

$$\left(\frac{\partial U}{\partial V} \right)_{T,N} = T \frac{p}{T} - p = 0$$

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$F = U - TS$$

$$dF = -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\Phi \equiv F + PV$$

$$d\Phi = -SdT + VdP \Rightarrow \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

enthalpy

$$H \equiv W \equiv U + PV$$

$$dH = TdS + VdP \Rightarrow T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$dU = T dS - P dV \Rightarrow dS = \frac{1}{T} dU + \frac{P}{T} dV$$

$$\downarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \Leftrightarrow T = T(U, V)$$

$$\downarrow \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_U \Leftrightarrow P = P(U, V)$$

$$dU = \underbrace{S}_{\substack{\text{extensive} \\ \text{properties}}} dT - \underbrace{P}_{\substack{\text{intensive} \\ \text{properties}}} dV + \underbrace{\mu}_{\substack{\text{intensive} \\ \text{properties}}} dN - \underbrace{M}_{\substack{\text{intensive} \\ \text{properties}}} dB - \underbrace{P}_{\substack{\text{intensive} \\ \text{properties}}} dE \dots$$

$S, V, N, U, E \dots$
 P, T, μ

$$d\Phi = -S dT + V dP + \mu dN$$

$$\Phi(T, P, N) = N f(T, P)$$

$$\mu = \left(\frac{\partial \Phi}{\partial N} \right)_{P, T} = f(T, P) \Rightarrow \boxed{\Phi = \mu(P, T) N}$$

$$dU = T dS - P dV + \mu dN$$

$$dF = -S dT - P dV + \mu dN$$

$(S, T), (P, V), (\mu, N)$ conjugate pairs

$$F(T, V, N) = U - TS \quad T = \frac{\partial U}{\partial S}$$

$$T \left(\frac{\partial S}{\partial T} \right)_X = \left(\frac{\partial Q}{\partial T} \right)_X = C_X : \text{heat capacity}$$

(extensive quantity)

$$\frac{C}{N} \equiv \text{specific heat capacity}$$

X: process

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_{V,N} = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

$$dU = T dS - P dV + \mu dN$$

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_{P,N} = T \left(\frac{\partial S}{\partial T} \right)_{P,N} = \left(\frac{\partial H}{\partial T} \right)_{P,N}$$

$$dH = T dS + V dP + \mu dN$$

Example Ideal gas

$$PV = NkT$$

$$U = \frac{3}{2} NkT = \frac{3}{2} PV$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} Nk$$

$$C_p =$$

$$U(P, T, N) = \frac{3}{2} NkT$$

$$dU = TdS - PdV$$

$$dQ = dU + PdV \iff$$

$$\left. \left(\frac{dQ}{dT} \right)_{P, N} = \left(\frac{\partial U}{\partial T} \right)_{P, N} + P \left(\frac{\partial V}{\partial T} \right)_{P, N} \right\}$$

$$= \frac{3}{2} Nk + P \frac{Nk}{P}$$

$$V(P, N, T) = \frac{NkT}{P}$$

$$C_p = \frac{5}{2} Nk$$

For ideal gas $PV = NkT$

$$C_p = C_v + P \left(\frac{\partial V}{\partial T} \right)_{P, N}$$

$$\gamma = \frac{5}{3} = \frac{\frac{5}{2} Nk}{\frac{3}{2} Nk} = \frac{C_p}{C_v}$$

HW

