First Law:

$$dU = dQ + dW$$

$$dU = TdS - PdV \Rightarrow \text{Holds for irreversible process also}$$

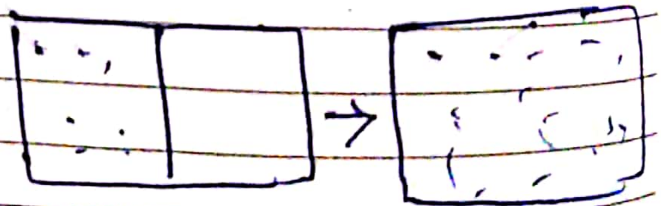
$$U = U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left.\begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_V \\ P &= -\left(\frac{\partial U}{\partial V}\right)_S \end{aligned}\right\} \Rightarrow \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$

Joule Expansion:

Isothermal Expansion.



$$\Delta S = \int_{V_1}^{V_2} \frac{dQ}{T} = \int_{V_1}^{V_2} \frac{dU + PdV}{T} = R\ln\left(\frac{V_2}{V_1}\right)$$

$$V_2 > V_1$$

$$\Rightarrow \Delta S > 0$$

Entropy of ideal gas:

$$T\,ds = C_v\,dT + P\,dv$$

$$\Rightarrow ds = C_v \frac{dT}{T} + \frac{R\,dv}{v}$$

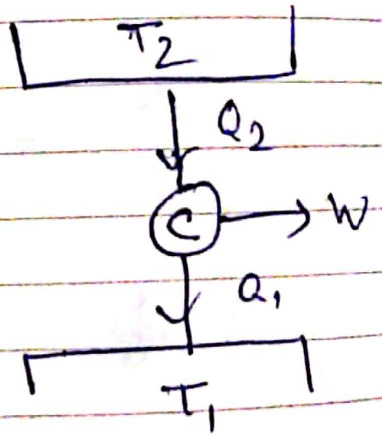
$$\Rightarrow S_2 - S_1 = C_v \ln\left(T_2/T_1\right) + R \ln\left(v_2/v_1\right)$$

HW.

Available Energy:

Carnot Engine

$T_2 > T_1$



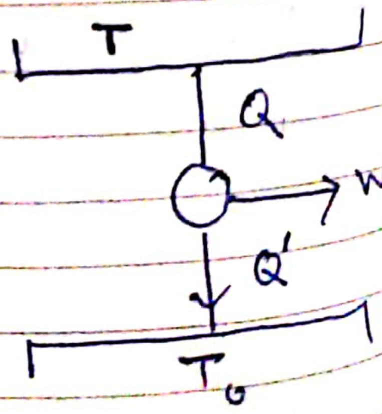
$$\eta = 1 - \frac{T_1}{T_2}$$

$$W_1 = Q\left(1 - \frac{T_0}{T_1}\right)$$

$$W_2 = Q\left(1 - \frac{T_0}{T_2}\right)$$

$T_1 > T_2$

$\Rightarrow W_1 > W_2$



$$LE = W_1 - W_2 = Q T_0\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= T_0 \Delta S$$

Thermal death.

Thermodynamic Relations: Maxwell's Relation.

$$dU = Tds - pdv$$

Internal energy

Natural variable $T, p \rightarrow$ intensive.

$S, V \rightarrow$ Extensive.

$$U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

Define. $H = U + PV$ Enthalpy.

$$\Rightarrow dH = dU + PdV + Vdp$$

$$= TdS + Vdp \qquad H(S, P)$$

Helmholtz $F = U - TS$

$$dF = TdS - pdV - TdS - SdT$$

$F = F(T, V)$

$$= -SdT - pdV$$

Gibb's Free Energy:

$$G = H - TS$$

$$\Rightarrow dG = dH - TdS - SdT$$

$$= TdS + vdp - TdS - SdT$$

$$= -SdT + vdp$$

$$G = G(T, P)$$

1. Internal Energy:

$$dU = TdS - pdv$$

For isochoric process $dv = 0$.

$$\Rightarrow dU = TdS = dQ_r = C_v dT$$

$$\Rightarrow \Delta U = \int_{T_1}^{T_2} C_v dT$$

2. Enthalpy: $dH = TdS + vdp$

For isobaric process $dp = 0$

$$\Rightarrow dH = TdS = dQ_r = C_p dT$$

$$\Rightarrow \Delta H = \int_{T_1}^{T_2} dT\, C_p$$

3. Helmholtz Func.

$$dF = -SdT - pdV$$

For isothermal process. $dT = 0$.

$$\Rightarrow df = -pdV$$

$$\Delta F = -\int_{V_1}^{V_2} pdV$$

4. Gibbs Free energy:

$$dG = -SdT + Vdp.$$

For isothermal process $dT = 0$.

$$dG = \int V dp$$