$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)\right)_T = \underline{\frac{1}{T}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T}$$

$$\parallel$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T}\Big[\underbrace{\frac{1}{T}\Big[\left(\frac{\partial U}{\partial V}\right)_T + P\Big]}_{h(T)}\Big]\right)_V$$

$$f(T) = \frac{1}{T} \qquad g(T) \rightarrow \left(\frac{\partial U}{\partial V}\right)_T + P$$

$$= \frac{\partial f}{\partial T}\cdot g(T) + \frac{\partial g}{\partial T}\cdot f(T)$$

$$= -\frac{1}{T^2}\Big[\left(\frac{\partial U}{\partial V}\right)_T + P\Big] + \frac{1}{T}\Big[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\Big]$$

$$\parallel$$

$$\rightarrow \underline{\frac{1}{T}\left(\frac{\partial}{\partial V}\cancel{\left(\frac{\partial U}{\partial T}\right)_V}\right)_T} = -\frac{1}{T^2}\Big[\left(\frac{\partial U}{\partial V}\right)_T + P\Big] + \frac{1}{T}\Big[\left(\frac{\partial P}{\partial T}\right)_V + \underline{\cancel{\left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V}}\Big]$$

$$0 = -\frac{1}{T^{\cancel{2}}}\Big[\underline{\left(\frac{\partial U}{\partial V}\right)_T} + P\Big] + \cancel{\frac{1}{T}}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right) - P} \; *$$

---

① For ideal gas $\quad PV = NRT$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right) - P \qquad \left(P = \frac{NRT}{V}\right)$$

$$= \underbrace{T\cdot\frac{NR}{V}}_{P} - P = P - P = 0$$

② For real gas (e.g. vdW)

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{NRT}{V-Nb} - \frac{N^2a}{V^2} \quad (v = V/N)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right) - P$$

$$= T\left[\frac{NR}{V-Nb}\right] - P = \cancel{P} + \frac{N^2a}{V^2} - \cancel{P} = \frac{N^2a}{V^2}$$

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

$$= C_V\,dT + \frac{N^2a}{V^2}\,dV$$

$$\rightarrow \Delta U = \int dU = \int_{T_i}^{T_f} C_V\,dT + \int_{V_i}^{V_f} \frac{N^2a}{V^2}\,dV$$

$$= \int_{T_i}^{T_f} C_V(T)\,dT + N^2a\left(\frac{1}{V_i} - \frac{1}{V_f}\right)$$

---

*. heat capacity C_V vs. C_P.

$$đQ = dU - đW = dU + PdV$$

$$\begin{cases} đQ_V \equiv C_V \cdot dT \\ đQ_P \equiv C_P \cdot dT = dU + PdV \end{cases}$$

$$\hookrightarrow \underbrace{C_V \cdot dT}_{U(V,T)} + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T \cdot dV}_{U(V,T)} + PdV$$

$$\rightarrow C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$= C_V + \left(\frac{\partial V}{\partial T}\right)_P \Big[\underbrace{\left(\frac{\partial U}{\partial V}\right)_T + P}_{T\left(\frac{\partial P}{\partial T}\right)_V - P}\Big]$$

$$= C_V + T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

*

For ideal gas : $PV = NRT$ or $P = \frac{NRT}{V}$ or $V = \frac{NRT}{P}$

$$\rightarrow C_P = C_V + T \cdot \frac{NR}{P} \cdot \frac{NR}{V} = C_V + NR$$

*. For General Case :

we know $\begin{cases} \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \& \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \\ \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1. \end{cases}$ *

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\rightarrow C_P = C_V - \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} = C_V + \frac{T \cdot V \cdot \alpha^2}{\kappa_T}$$

or $$C_{P,m} = C_{V,m} + \frac{TV\alpha^2}{N \cdot \kappa_T}$$

Obj. 5. Reversibility and Max work.

1. Possible and impossible processes.
2. Quasi-static Process. and Reversibility.
3. The maximum work theorem.

---

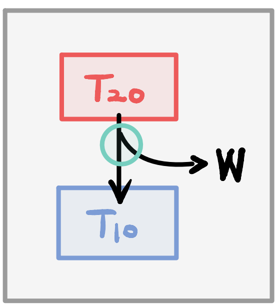
1. Possible and impossible processes.

Possible → $(\Delta S \geq 0)$ impossible → $(\Delta S < 0)$

Postulate I: There exists a function $S = S(U, V, \cdots N)$

$U, V, N \cdots$ tend to maximize S

two sys. const. V. N.



Isolated

$T_{20} > T_{10}$ follow

$$S = S_0 + C \ln (U / U_0)$$

$$U = C \cdot T$$

C ↓ heat capacity.

what's the max work that can be delivered?

Ans:

1> Energy conservation

Due to heat flow → $T_{1f} = T_{2f} = T_f$

$$\Delta U_2 = C(T_{20} - T_f) = \Delta U_1 + W$$

$$= C(T_f - T_{10}) + W$$

$$\rightarrow W = C(T_{10} + T_{20} - 2T_f)$$

2> Also consider ΔS (at least $\Delta S \geq 0$)

$$\Delta S = \Delta S_1 + \Delta S_2 \geq 0$$

$$\boxed{\begin{array}{l} S = S_0 + C\ln(U/U_0) \\ U = C \cdot T \end{array}}$$

$$= S_{1f} - S_{10} + S_{2f} - S_{20}$$

$$= \cancel{S_{10}} + C\ln\frac{CT_f}{U_{10}} - \left(\cancel{S_{10}} + \cancel{C\ln\frac{CT_{10}}{U_{10}}}\right)$$

$$+ \cancel{S_{20}} + C\ln\frac{CT_f}{U_{20}} - \left(\cancel{S_{20}} + \cancel{C\ln\frac{CT_{20}}{U_{20}}}\right)$$

$$= C\ln\frac{\cancel{C}T_f}{\cancel{C}T_{10}} + C\ln\frac{\cancel{C}T_f}{\cancel{C}T_{20}} = C\ln\frac{T_f^2}{T_{10}T_{20}} = 2C\ln\underbrace{\frac{T_f}{\sqrt{T_{10}T_{20}}}}_{\geq 1} \geq 0$$

$$\rightarrow T_f \geq \sqrt{T_{10}T_{20}}$$

overall $\rightarrow$ $\begin{cases} W = C(T_{10} + T_{20} - 2T_f) & \text{Energy Conservation} \\ T_f \geq \sqrt{T_{10}T_{20}} & \text{possible } (\Delta S \geq 0) \end{cases}$

to max out W, should minimize T_f

However, we also need to have $T_f \geq \sqrt{T_{10}T_{20}}$

thus. $(T_f)_{min} = \sqrt{T_{10} T_{20}}$

$\rightarrow W_{max} = C(T_{10} + T_{20} - 2\sqrt{T_{10} T_{20}})$