Lecture 8/23/2023

- Conservation of Energy

$$dU = dQ - dW$$

energy absorbed work done

$U(p, V)$

$p, V, T, S, U, \dots$

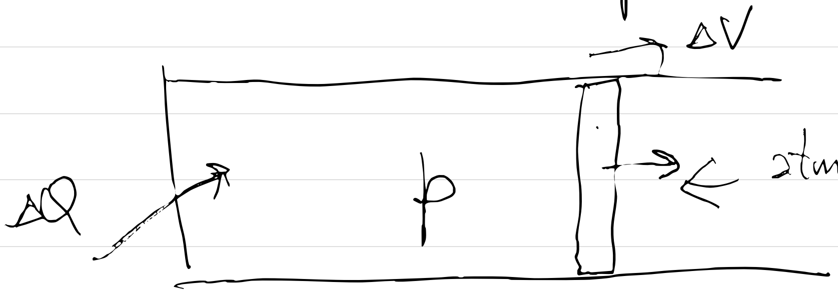
$$dU = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_p dV$$

$$\partial^2_{xy} f = \partial^2_{yx} f$$

$$\frac{\partial}{\partial V}\underbrace{\left(\frac{\partial U}{\partial p}\right)_V} = \frac{\partial}{\partial p}\underbrace{\left(\frac{\partial U}{\partial V}\right)_p}$$

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

reversible $\quad dW = p\,dV$



$$dU = dQ - p\underbrace{dV}$$

$$\underbrace{\left(\frac{\partial U}{\partial T}\right)_V} = \underbrace{\left(\frac{\Delta Q}{\Delta T}\right)_V}$$

$$\underbrace{C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p}$$

$\boxed{H = U + pV}$ enthalpy

$$dH = dU + p\,dV + V\,dp$$

$$= dQ - \cancel{p\,dV} + \cancel{p\,dV} + V\,dp$$

$$\left(\frac{\Delta Q}{\Delta T}\right)_p = \left(\frac{\Delta H}{\Delta T}\right)_p \rightarrow \left(\frac{\partial H}{\partial T}\right)_p$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$= \left(\frac{\partial U}{\partial T}\right)_p + \underline{p\left(\frac{\partial V}{\partial T}\right)_p}$$

$$pV = NkT \Rightarrow U = C_v T$$

$$U(T, V(T,p))$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \cancelto{0}{\left(\frac{\partial U}{\partial V}\right)_T} \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = C_V + p\left(\frac{\partial V}{\partial T}\right)_p$$

$\nwarrow Nk/p$

$pV = NkT$

$$\boxed{C_p - C_V = Nk_B}$$

Ideal gas.

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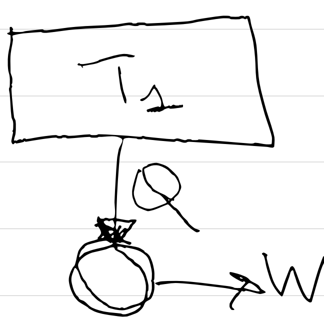
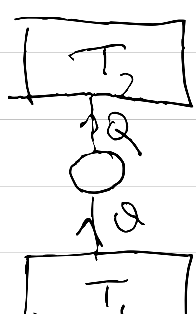
a)



$Q = W$

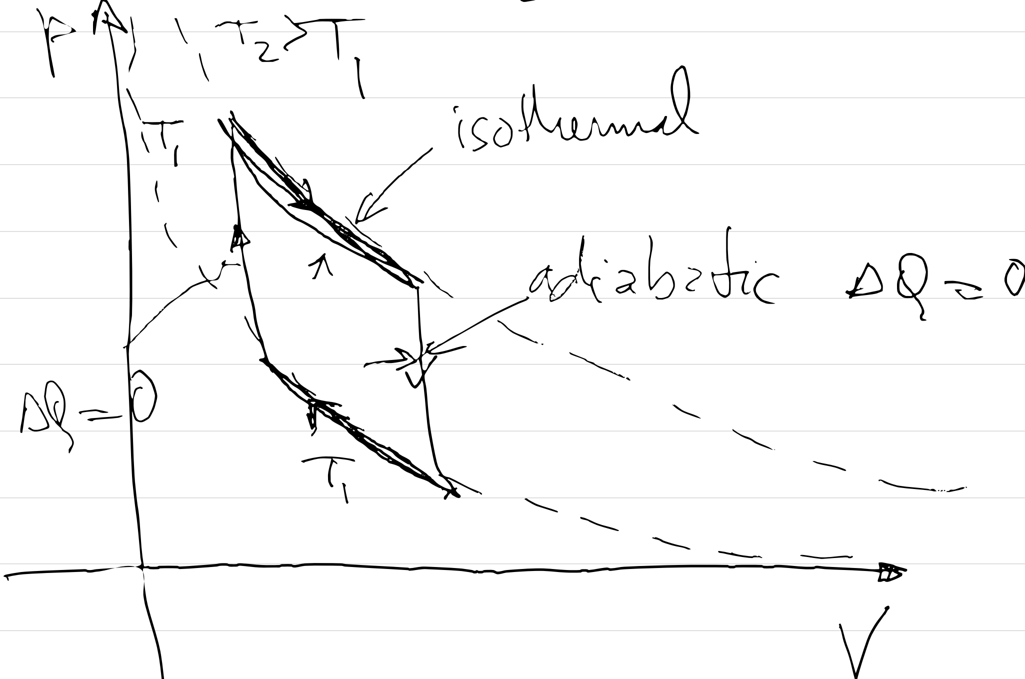
$W \leq 0$

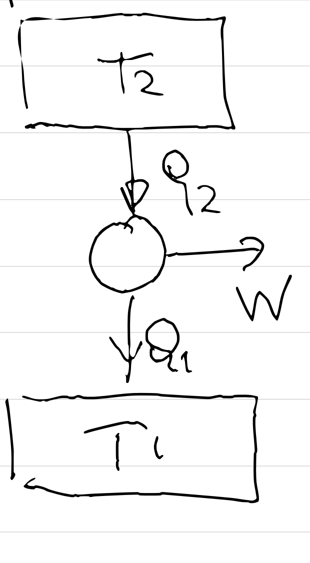


$T_2 > T_1$

$Q < 0$

Carnot's engine

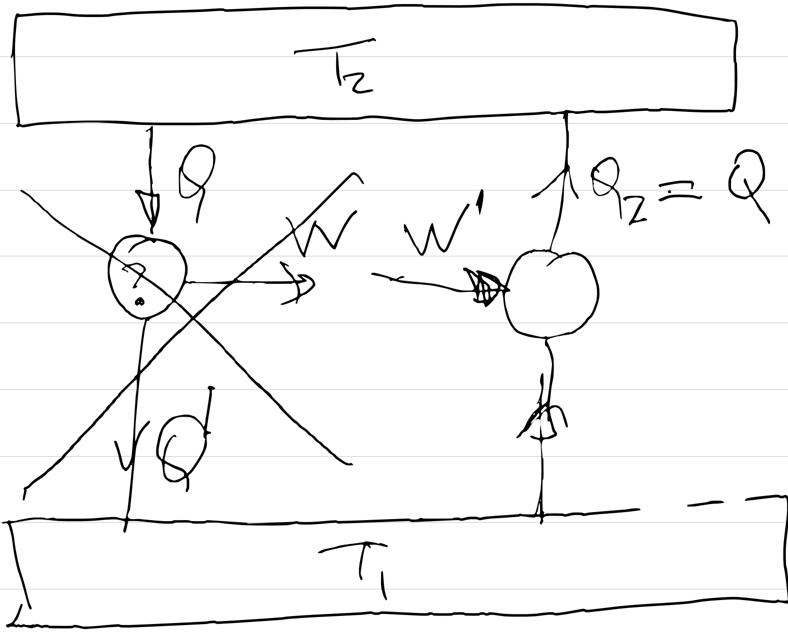




$$W = Q_2 - Q_1 \neq 0$$

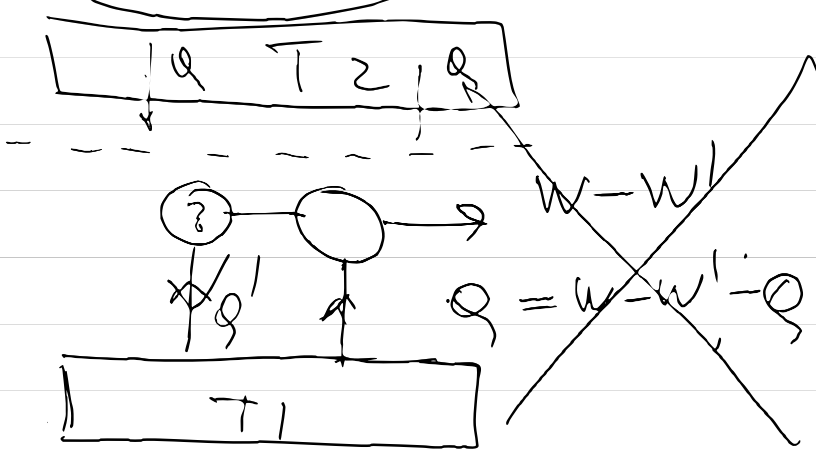
$$\eta = \frac{W}{Q_2} < 1$$

$$\eta = 1 - Q_1/Q_2$$



$$\frac{W}{Q} = \eta > \eta_{carnot} = \frac{W'}{Q_2}$$

$$W > W'$$

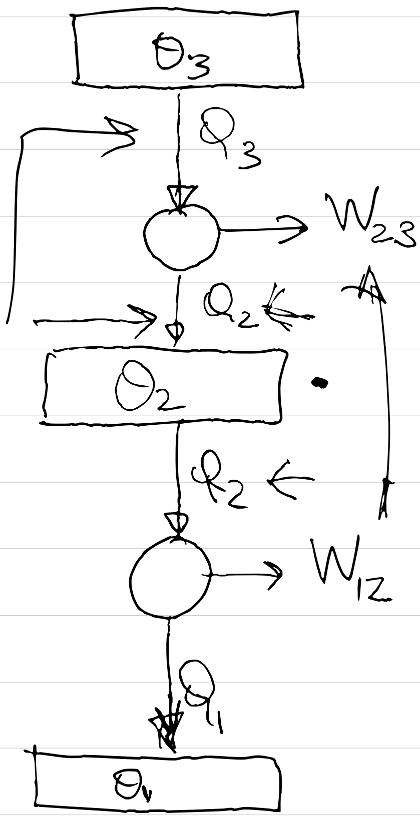


Absolute temperature

$$\eta = \frac{W}{Q_2} = 1 - \frac{Q_1}{Q_2} = 1 - \underbrace{\frac{\theta_1}{\theta_2}}_{>0}$$

$\eta < 1$ $\qquad$ $\theta_{1,2} > 0$

$$Q_3 - Q_2 = W_{23}$$



$$W_{23} = \eta_{23} \cdot Q_3$$

$$W_{12} = \eta_{12} Q_2$$

$$W_{13} = \eta_{13} Q_3$$

$$\eta_{13} = 1 - \frac{\theta_1}{\theta_3}$$

$$\eta_{13} = \frac{W_{13}}{Q_3} = \frac{W_{12} + W_{23}}{Q_3}$$

$$\begin{cases} W_{23} = \eta_{23} Q_3 \\ W_{12} = \eta_{12} Q_2 \end{cases}$$

$$Q_3 - Q_2 = W_{23}$$

$$= \eta_{23} Q_3$$

$$1 - \frac{Q_2}{Q_3} = \eta_{23}$$

$$= 1 - \frac{\theta_2}{\theta_3}$$

$$W_{13} = \eta_{13} Q_3$$

$$\eta_{13} = 1 - \frac{\theta_1}{\theta_3}$$

$$\eta_{13} = \frac{W_{13}}{Q_3} = \frac{W_{12} + W_{23}}{Q_3} = \eta_{12} \frac{Q_2}{Q_3} + \eta_{23}$$

$$= \left(1 - \frac{\theta_1}{\theta_2}\right) \frac{Q_2}{Q_3} + \left(1 - \theta_2/\theta_3\right)$$

$$= \left(1 - \frac{\theta_1}{\theta_2}\right) \frac{\theta_2}{\theta_3} + 1 - \theta_2/\theta_3$$

$$= \cancel{\frac{\theta_2}{\theta_3}} - \frac{\theta_1}{\theta_3} + 1 - \cancel{\frac{\theta_2}{\theta_3}} = \boxed{1 - \theta_1/\theta_3}$$

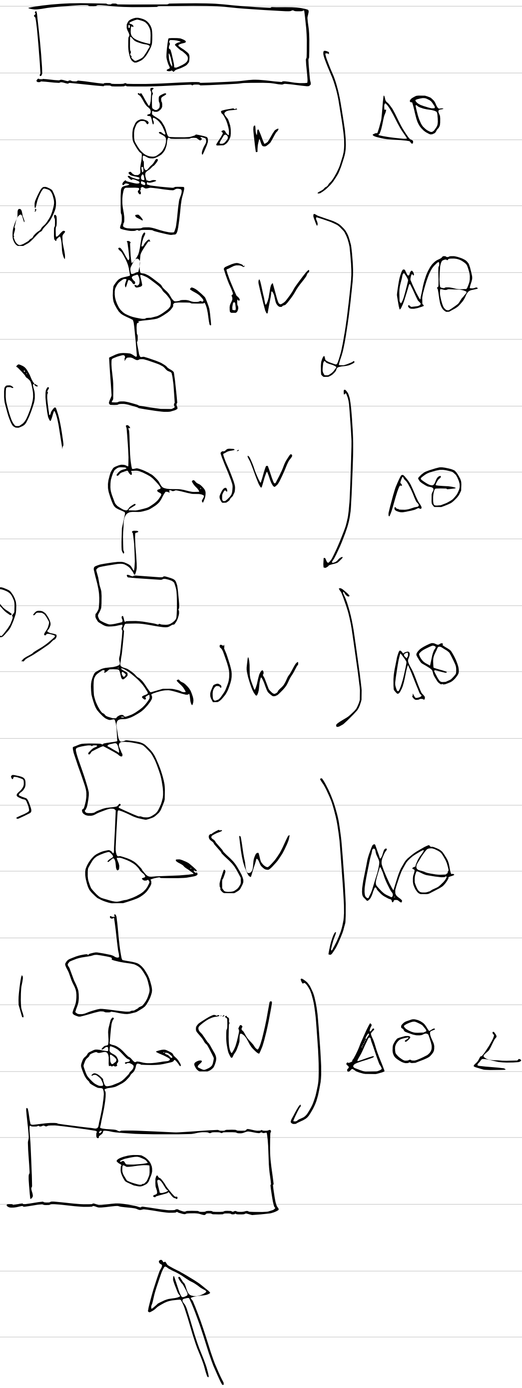
$$\left.\begin{aligned} W_{23} &= \eta_{23} \cdot Q_3 \\ W_{12} &= \eta_{12} Q_2 \end{aligned}\right\}$$ assumpt. $W_{23} = W_{12}$

$$\eta_{23} Q_3 = \eta_{12} Q_2$$

$$\left(1 - \frac{\theta_2}{\theta_3}\right) \frac{Q_3}{Q_2} = \left(1 - \frac{\theta_1}{\theta_2}\right)$$

$$\left(1 - \frac{\theta_2}{\theta_3}\right) \frac{\theta_3}{\theta_2} = 1 - \frac{\theta_1}{\theta_2}$$

$$\underbrace{(\theta_3 - \theta_2)}\frac{1}{\cancel{\theta_2}} = \overbrace{\frac{\theta_2 - \theta_1}{\cancel{\theta_2}}}$$


θB
δw
ΔΘ
θ4
δW
ΔΘ
θ4
δW
ΔΘ
θ3
dW
ΔΘ
θ3
δW
ΔΘ
θ1
δW
ΔΘ
θA


pV=NkT
Θ
T

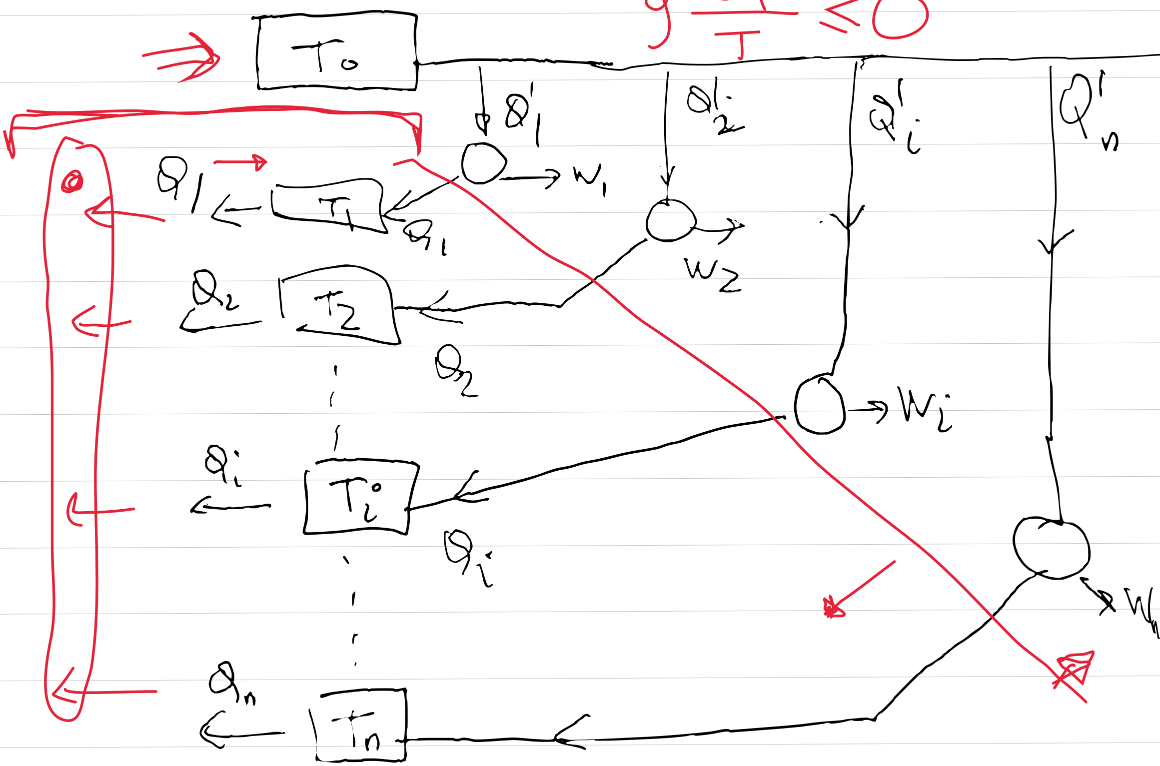
Clausius theorem

For a cyclic transformation throughout which the temperature is defined:

$$\boxed{\oint \frac{dQ}{T} \leq 0}$$

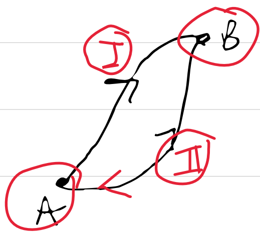
(= if reversible)

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



$$\boxed{\sum_j Q'_j \leq 0} \qquad Q'_j / Q_j = T_0 / T_i \quad \Rightarrow \sum_j \frac{Q_j}{T_j} \leq 0$$

If reversible we can run it in reverse $\Rightarrow \oint \frac{dQ}{T} \geq 0 \Rightarrow \oint \frac{dQ}{T} = 0$

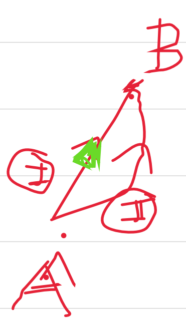


indep. of path!

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

S: function of state.

All these is derived from some basic principles. No need to understand the underlying physics.



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

$\boxed{S(B) \geq S(A)}$ isolated

$$\boxed{dU = \underbrace{T\,dS}_{dQ} - p\,dV} \qquad U(S,V)$$

$$\Rightarrow \quad p = -\left(\frac{\partial U}{\partial V}\right)_S \; ; \qquad T = \left(\frac{\partial U}{\partial S}\right)_V$$

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

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

$$= -p + T\left(\frac{\partial S}{\partial V}\right)_T$$

Free energy

F $\quad A = U - TS$ thermodynamic quantity.

$$dA = -S\,dT - p\,dV \qquad A(T,V)$$

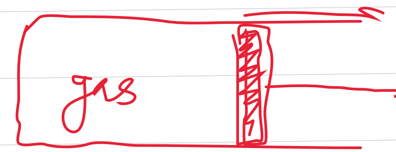
$$(\partial S/\partial V)_T = (\partial P/\partial T)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V}$$

<u>ideal gas</u>

$$pV = NkT \qquad \text{(definition).}$$

$$(\partial p/\partial T)_V = \frac{Nk}{V} = p/T$$



$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -p + T\frac{p}{T} = 0 \qquad \checkmark$$

—o—

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$ <u>thermal expansion</u>

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$ isothermal compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$ adiabatic compressibility

$$\boxed{C_p - C_V = \frac{TV\alpha^2}{\kappa_T}}$$

Nk

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad ; \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

α, κ_T, C_p use $(p, T) \Rightarrow U(T, p(V,T))$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$= \left(\frac{\partial H}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$p(T, V(p,T))$$

$$\left(\frac{\partial p}{\partial T}\right)_p = 0 = \left(\frac{\partial p}{\partial T}\right)_V + \underbrace{\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}$$

$$\left(\frac{\partial p}{\partial p}\right)_T = 1 = \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \underbrace{-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p} = \boxed{-\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T}}$$

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial p}\right)_T \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T}$$

$$= p\alpha V + \underbrace{\left(\frac{\partial U}{\partial p}\right)_T} \frac{\alpha \cancel{V}}{(-\cancel{V}\kappa_T)}$$

$$= p\alpha V + \left(\frac{\partial U}{\partial p}\right)_T \frac{\alpha \cancel{V}}{(-\cancel{V}\kappa_T)}$$

$$C_p - C_v = \alpha p V - \frac{\alpha}{\kappa_T}\left(\frac{\partial U}{\partial p}\right)_T$$

S, V T, p

U, H, A, G

T, V p, T

$$G = U - ST + pV$$

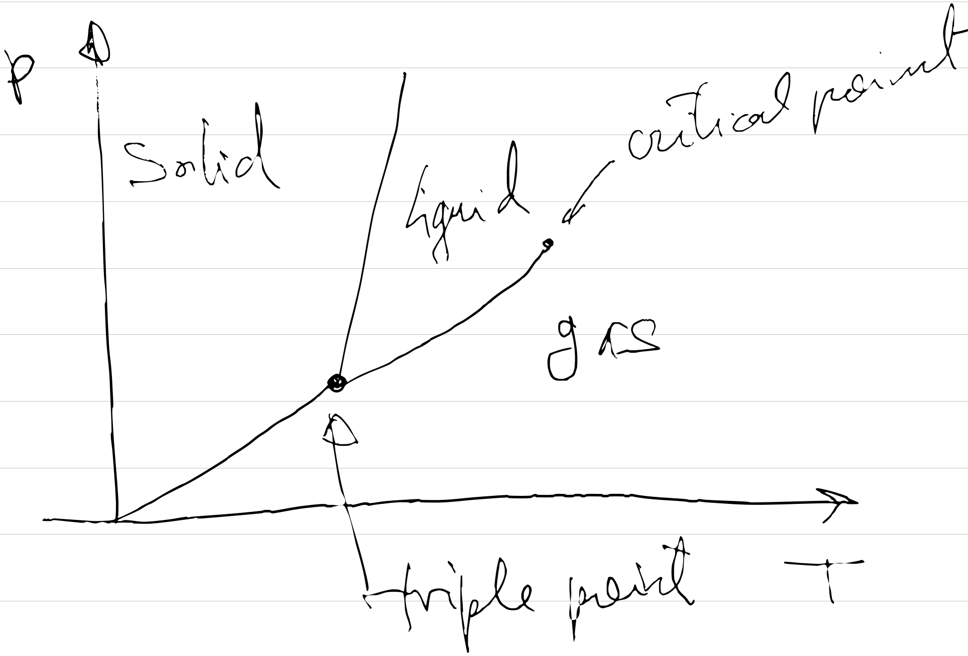
$$\boxed{dG = -S\,dT + V\,dp}$$

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

$$\boxed{C_p - C_V} = \cancel{\alpha p V} - \frac{\alpha T}{\kappa_T}\left(\frac{\partial S}{\partial p}\right)_T + \cancel{\frac{\alpha p}{\kappa_T}(-\kappa_T V)}$$

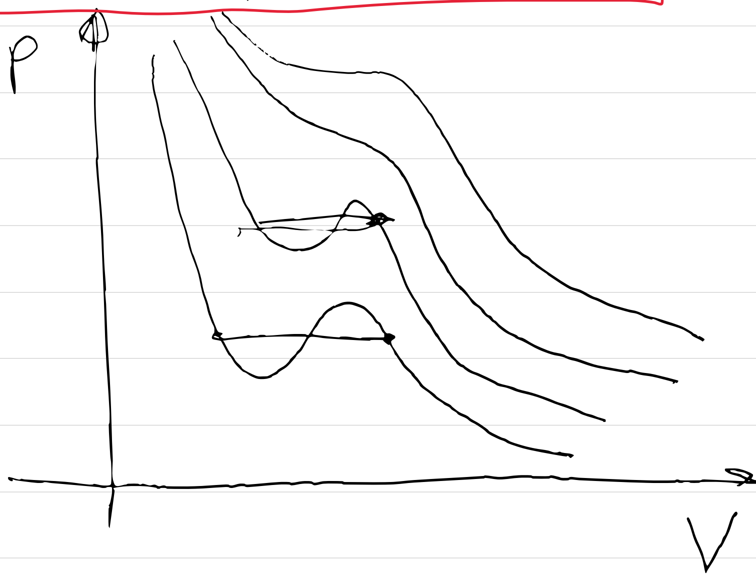
$$= + \frac{\alpha T}{\kappa_T} \times \left(+\frac{\partial V}{\partial T}\right)_p = \boxed{\frac{\alpha^2 V T}{\kappa_T}} \checkmark$$

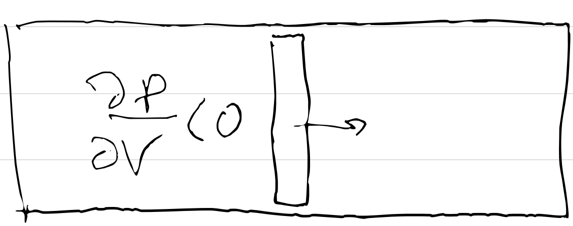
Phase transitions



Van der Waals eq. of state

$$\boxed{(V-b)(p+a/V^2) = RT}$$





Van der Waals

$$P = -\frac{a}{V^2} + \frac{RT}{V-b} \;;\; \frac{\partial p}{\partial V} = \frac{2a}{V^3} - \frac{RT}{(V-b)^2} \;;\; \frac{\partial^2 p}{\partial V^2} = -\frac{6a}{V^4} + \frac{2RT}{(V-b)^3}$$

$$\left.\begin{array}{l} \dfrac{RT_c}{(V_c-b)^2} = \dfrac{2a}{V_c^3} \\[2ex] \dfrac{RT_c}{(V_c-b)^3} = \dfrac{3a}{V_c^4} \end{array}\right\} \quad \left.\begin{array}{l} \dfrac{2\cancel{a}}{\cancel{V_c^3}} = \dfrac{3\cancel{a}(V_c-b)}{V_c^{\cancel{4}}} \\[2ex] 2V_c = 3V_c - 3b \end{array}\right\}$$

$$\boxed{\begin{array}{l} V_c = 3b \\[1ex] RT_c = \dfrac{2a}{27b^3}4b^2 = \dfrac{8}{27}\dfrac{a}{b} \\[2ex] P_c = -\dfrac{a}{9b^2} + \dfrac{8a}{27b^2 2} = \dfrac{a}{27b^2} \end{array}}$$

$V = \bar{V} V_c$

$p = \bar{p}\, p_c$

$T = \bar{T}\, T_c$

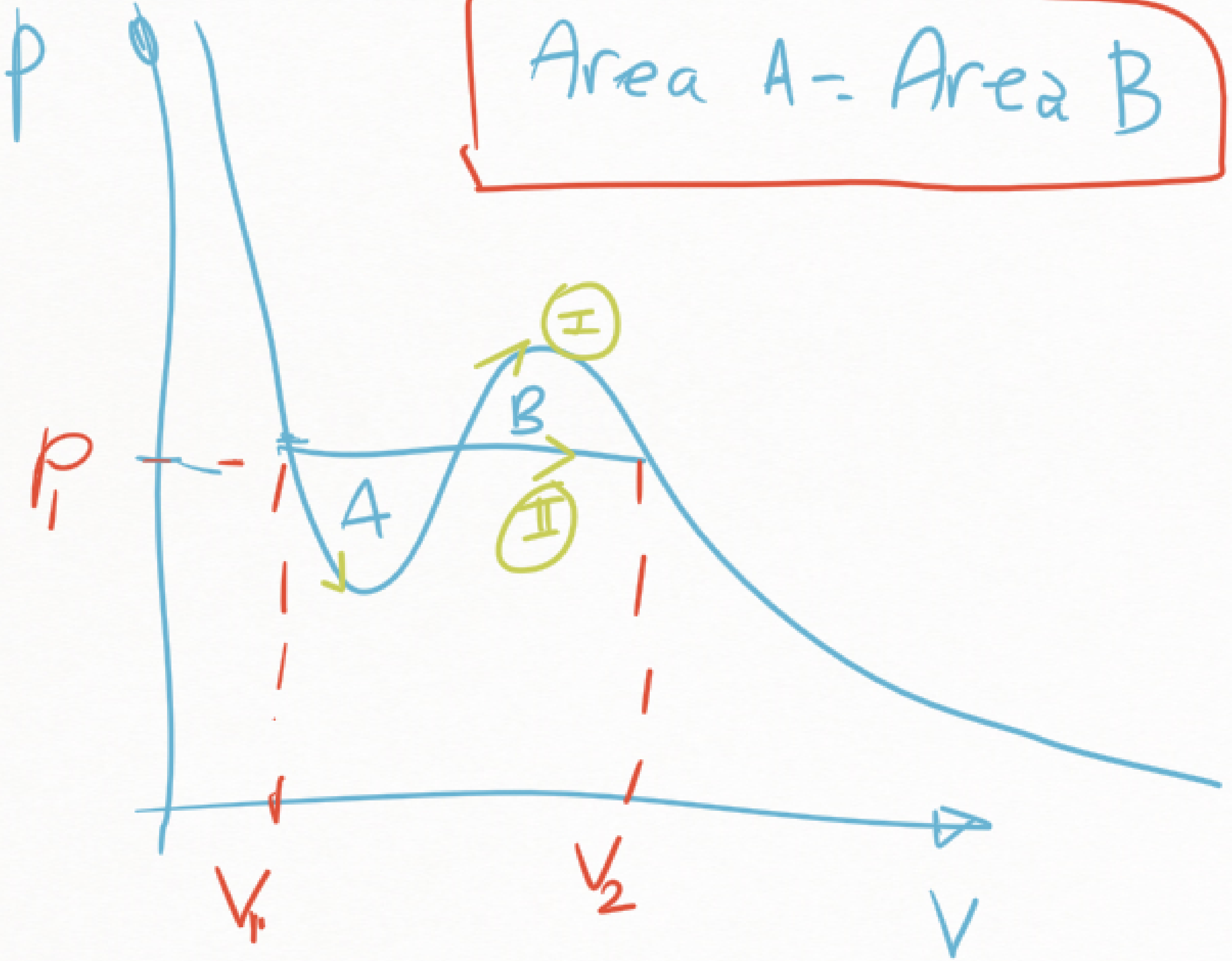
$$\cancel{b}\,(3\bar{V}-1)\left(\frac{\cancel{a}}{27\cancel{b}}\bar{p} + \frac{\cancel{a}}{9\cancel{b}\bar{V}^2}\right) = \frac{8\cancel{a}}{27\cancel{b}}\bar{T}$$

$$\boxed{(3\bar{V}-1)\left(\bar{p} + \frac{3}{\bar{V}^2}\right) = 8\bar{T}}$$

Universal form of Van der Waals eqn.

Maxwell construction

$\boxed{\text{Area } A = \text{Area } B}$



$dA = -S\,dT - p\,dV$

$$A_2 - A_1 = -\int_{V_1}^{V_2} p\,dV \quad \text{I}$$

$$= -p_1 (V_2 - V_1) \quad \text{II}$$