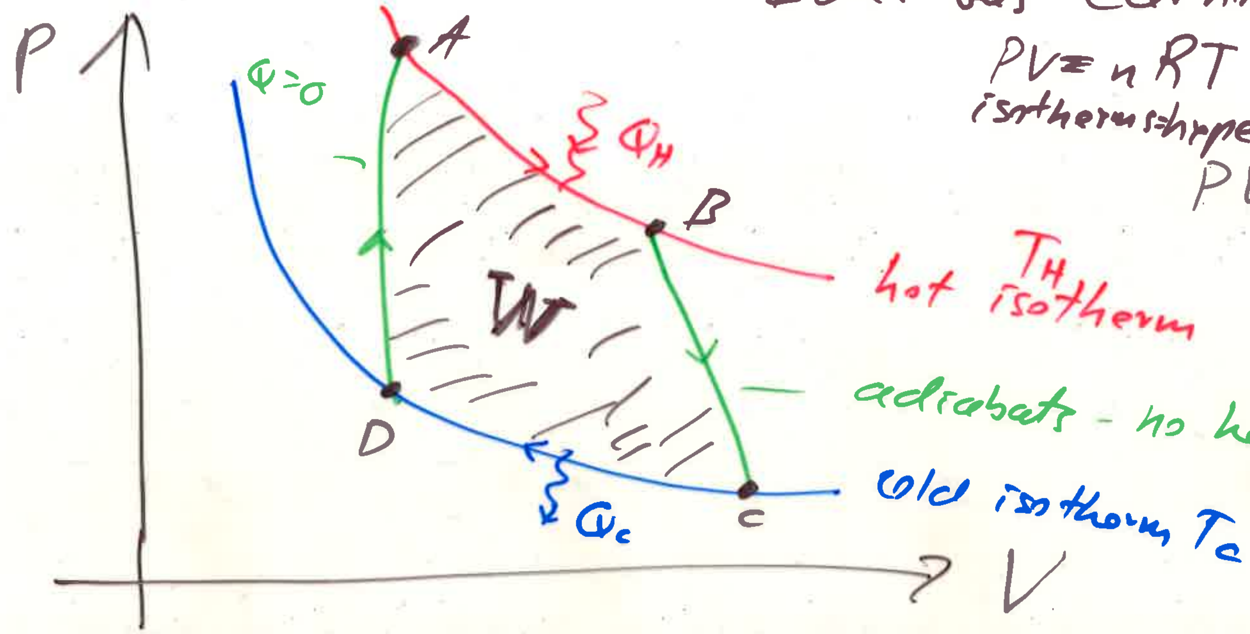
Ideal Gas Carnot cycle

$PV = nRT$

isotherms hyperbolae

$PV = \text{const}$



adiabats ideal gas $\boxed{PV^{\gamma} = \text{constant}}$

monatomic $\gamma = \frac{5}{3}$ diatomic $\gamma = \frac{7}{5}$

$$\eta_{real} = \frac{Q_H' - Q_C'}{Q_H'} < \eta_{carnot} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = \boxed{1 - \frac{T_C}{T_H}}$$

Heat Capacity : $\left(\frac{\partial Q}{\partial T}\right)_{path}$

Food Calorie

$1\,Cal = 1000\,cal = 1\,kcal$

e.g. water $C_V \approx C_p = \frac{1\,cal}{g \cdot {}^\circ C} = \frac{1\,cal}{g \cdot K}$

$$dQ = dU + PdV \; (+\mu dN) \quad (1^{st}\ law)$$

Hold N fixed

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_{VN} = \left(\frac{\partial U}{\partial T}\right)_{VN} \qquad dV = 0$$

$$c_V = \frac{C_V}{\text{mass}} \quad \text{or} \quad \frac{C_V}{n} \leftarrow \#\text{ moles}$$

↑ intensive

$$C_p = \left(\frac{\partial U}{\partial T}\right)_{pN} + p\left(\frac{\partial V}{\partial T}\right)_{pN}$$

For an ideal gas $\quad U = U(T)$

$$\left(\frac{\partial U}{\partial T}\right)_{VN} = \left(\frac{\partial U}{\partial T}\right)_{pN} = \frac{dU}{dT}$$

$$C_p = C_V + p\left(\frac{\partial V}{\partial T}\right)_{pN} = C_V + \frac{pV}{T} = C_V + nR$$

$$C_p - C_V = nR$$

$$C_V = \frac{f}{2} nR$$

monatomic $\quad C_V = \frac{3}{2} nR = \frac{3}{2} N k_B$

diatomic $\quad C_V = \frac{5}{2} nR$

$$C_p = \frac{f}{2} nR + nR = \left(\frac{f+2}{2}\right) nR$$

monatomic $\Rightarrow C_p = \frac{5}{2} nR$

diatomic $\Rightarrow C_p = \frac{7}{2} nR$

$$\gamma = \frac{C_p}{C_V} \qquad U = \frac{f}{2} nRT$$

Proof that $PV^{\gamma} = \text{const.}$ for an ideal gas along an adiabat ($Q=0$)

C_v = specific heat

ideal $\Rightarrow$ $\underline{PV = nRT}$ $\Rightarrow$ $\boxed{dU = n\,C_v\,dT}$

adiabatic $\Rightarrow$ $đQ = 0$ $\Rightarrow$ 1st law $\Rightarrow$ $\boxed{dU = -p\,dV}$

$$d(PV = nRT) \to p\,dV + V\,dP = nR\,dT$$

$$p\,dV + V\,dp = \cancel{n}R\frac{dU}{\cancel{n}C_v} = \frac{R}{C_v}dU$$

$$p\,dV + V\,dP = -\frac{R}{C_v}p\,dV = -\frac{(C_p - C_v)}{C_v}p\,dV$$

$$= -(\gamma - 1)p\,dV$$

Divide PV

$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0 \qquad \text{integrate}$$

$$\gamma\ln(V) + \ln(P) = \text{constant}$$

$$\ln(V^{\gamma}) + \ln(P) = \text{constant}$$

$$\ln(PV^{\gamma}) = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

$\gamma > 1 \Rightarrow$ adiabats are steeper than the isotherms

Find Q_H (T_H = constant) $\Rightarrow dU = 0$

$\Rightarrow dQ = -dW$

$\Rightarrow Q_H = -W$

$$Q_H = \int_A^B p\,dV = \int_{V_A}^{V_B} \frac{nRT_H}{V}\,dV = nR\underline{T_H}\ln\left(\frac{V_B}{V_A}\right)$$

$$Q_c = -\int_C^D p\,dV = -nRT_c \ln\left(\frac{V_D}{V_c}\right) = nRT_c \ln\left(\frac{V_c}{V_D}\right)$$

$$W = Q_H - Q_c \; ; \quad \eta = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H}$$

Look at adiabats: PV^γ = constant, use $PV = nRT$

$\Rightarrow TV^{\gamma-1}$ = constant $\qquad \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_c}{V_D}\right)^{\gamma-1}$

$$\left.\begin{aligned} T_H V_B^{\gamma-1} &= T_c V_c^{\gamma-1} \\ T_H V_A^{\gamma-1} &= T_c V_D^{\gamma-1} \end{aligned}\right\} \text{divide} \Rightarrow \frac{V_B}{V_A} = \frac{V_c}{V_D}$$

$$Q_c = nRT_c \ln\left(\frac{V_c}{V_D}\right) = nRT_c \ln\left(\frac{V_B}{V_A}\right) = \frac{T_c}{T_H} Q_H$$

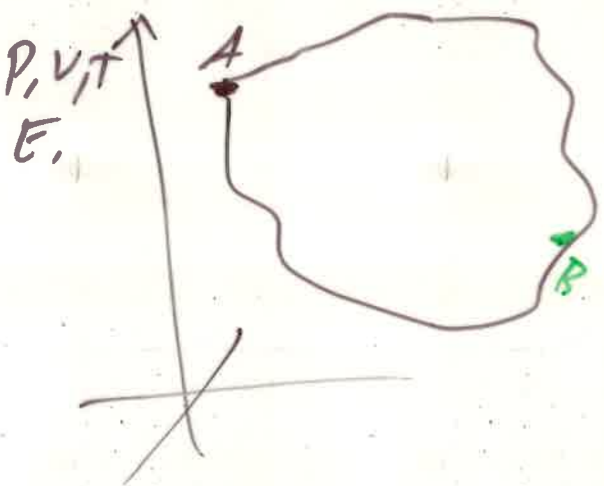
$$\frac{Q_H}{Q_c} = \frac{T_H}{T_c}\,, \quad \boxed{\eta = 1 - \frac{T_c}{T_H}} \qquad \frac{Q_H}{T_H} = \frac{Q_c}{T_c}$$

Carnot Engine (Reversible)

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \Longrightarrow \frac{Q_C}{T_C} = \frac{Q_H}{T_H} \equiv S \text{ entropy}$$

Need Clausius' Theorem



$$\oint \frac{dQ\,(\text{reversible})}{T} = 0$$

$\Longrightarrow$ There is a function of state called S

$$dS = \frac{dQ(\text{reversible})}{T}$$

$$\int_A^B \frac{dQ(\text{rever})}{T} = S_B - S_A = \Delta S$$

Thermodynamic Potentials

↙ natural variables

① Internal Energy : $U(V, S, N)$

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

$$\left(\frac{\partial U}{\partial V}\right)_{SN} = -P \quad \Big/ \quad \left(\frac{\partial U}{\partial S}\right)_{VN} = T \quad \Big/ \quad \left(\frac{\partial U}{\partial N}\right)_{VS} = \mu$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_{SN} dV + \left(\frac{\partial U}{\partial S}\right)_{VN} dS + \left(\frac{\partial U}{\partial N}\right)_{VS} dN$$

② Enthalpy : $H(P, S, N) = U + PV$

(Heat Function)

$$dH = dU + P\,dV + V\,dP$$

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

$$\left(\frac{\partial H}{\partial P}\right)_{SN} = V \quad \Big/ \quad \left(\frac{\partial H}{\partial S}\right)_{PN} = T \quad \Big/ \quad \left(\frac{\partial H}{\partial N}\right)_{PS} = \mu$$

③ Helmholtz Free Energy

$$A = F(V, T, N) = U - TS$$

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

$$\left(\frac{\partial F}{\partial V}\right)_{TN} = -P \quad \Big/ \quad \left(\frac{\partial F}{\partial T}\right)_{VN} = -S \quad \Big/ \quad \left(\frac{\partial F}{\partial N}\right)_{VT} = \mu$$

④ Gibbs Free Energy

$$G = U + PV - TS = G(P,T,N)$$

$$dG = VdP - SdT + \mu dN$$

$$\left(\frac{\partial G}{\partial P}\right)_{TN} = V \quad \left(\frac{\partial G}{\partial T}\right)_{PN} = -S \quad \left(\frac{\partial G}{\partial N}\right)_{PT} = \mu$$

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

$$\parallel \qquad\qquad \parallel$$

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