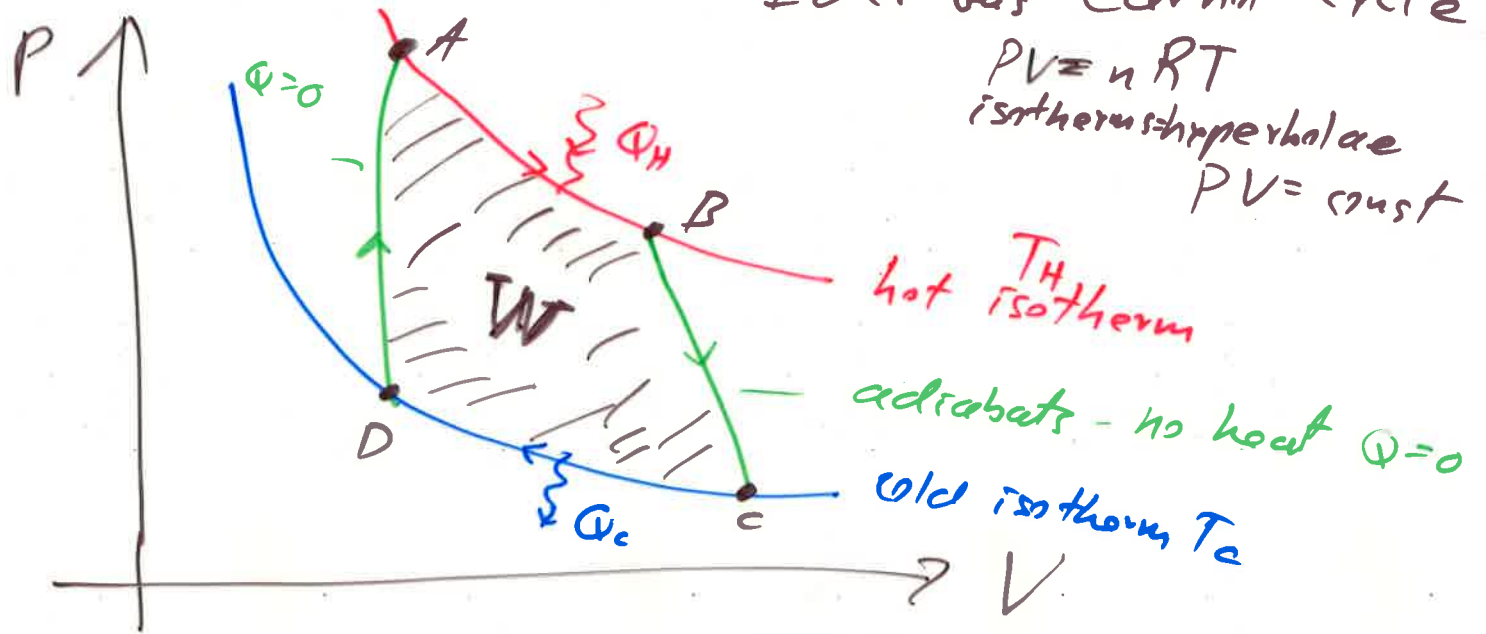


Ideal Gas Carnot cycle

$PV = nRT$
 isotherms = hyperbolae
 $PV = \text{const}$



adiabats ideal gas
 monatomic $\gamma = \frac{5}{3}$

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

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

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

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

ex. water
 $C_V \approx C_P \approx \frac{1 \text{ cal}}{9.0^\circ\text{C}} \rightarrow \frac{1 \text{ cal}}{9.0^\circ\text{K}}$

Food Calorie
 $1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$

$$dQ = dU + PdV \quad (\text{1st law})$$

(+ add N)

Hold N fixed

$$C_v = \left(\frac{\partial Q}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N} \quad dV=0$$

$$c_v = \frac{C_v}{\text{mass}} \quad \text{or} \quad \frac{C_v}{n} \leftarrow \# \text{ moles}$$

\uparrow intensive

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

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

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

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

$$C_p - C_v = nR$$

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

monatomic

diatomic

$$C_v = \frac{3}{2} nR = \frac{3}{2} Nk_B$$

$$C_v = \frac{5}{2} nR$$

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

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

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

$$\gamma = \frac{C_p}{C_v}$$

$$U = \frac{f}{2} nRT$$

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

ideal \Rightarrow $PV = nRT \Rightarrow dU = n C_v dT$

adiabatic $\Rightarrow dQ = 0 \Rightarrow$ 1st law $\Rightarrow dU = -pdV$

$d(PV = nRT) \Rightarrow pdV + VdP = nRdT$

$pdV + VdP = nR \frac{dU}{nC_v} = \frac{R}{C_v} dU$

$pdV + VdP = -\frac{R}{C_v} pdV = -\frac{(C_p - C_v)}{C_v} pdV$
 $= -(\gamma - 1)pdV$

Divide PV

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

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

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

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

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

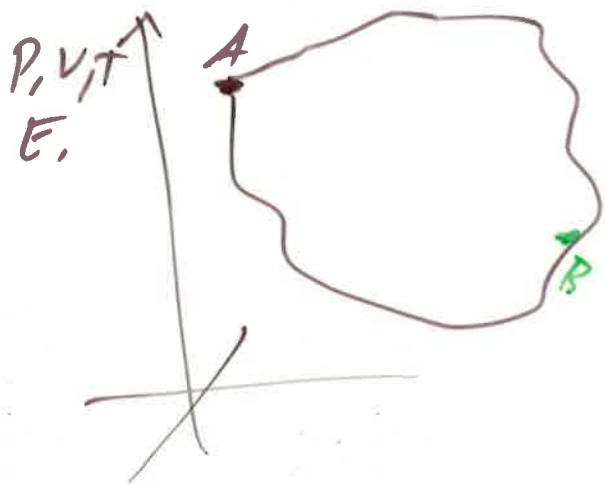
$\gamma > 1 \Rightarrow$ adiabats are steeper than the isotherms

Carnot Engine (Reversible)

$$\eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H}$$

$$\frac{Q_c}{Q_H} = \frac{T_c}{T_H} \implies \frac{Q_c}{T_c} = \frac{Q_H}{T_H} \equiv S \text{ entropy}$$

Need Clausius' Theorem



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

\implies there is a function of state called S

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

$$\textcircled{2} \int_A^B \frac{dQ(\text{revers})}{T} = S_B - S_A = \Delta S$$

Thermodynamic Potentials

① Internal Energy : $U(V, S, N)$ ↙ natural variables

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

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

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

② Enthalpy : $H(P, S, N) = U + PV$
(Heat Function)

$$dH = dU + PdV + VdP$$
$$= VdP + TdS + \mu dN$$

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

③ Helmholtz Free Energy

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

$$dF = -PdV - SdT + \mu dN$$

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

⊕ Gibbs Free Energy

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

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

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

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