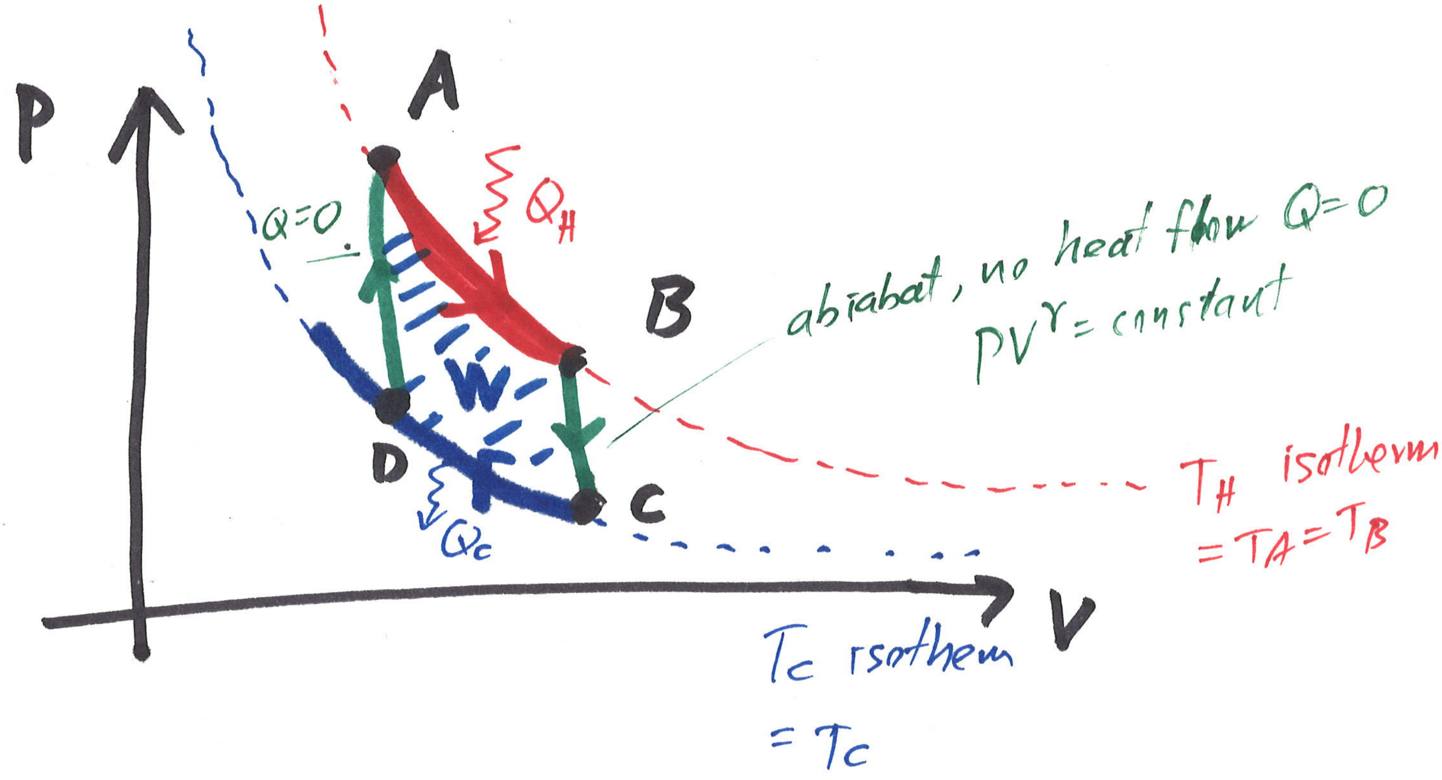
Ideal Gas Carnot Cycle

$PV = N k_B T$

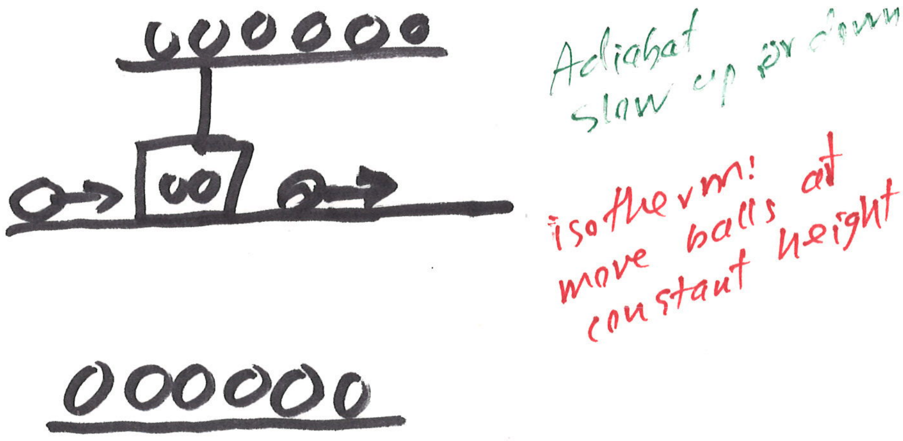


monatomic (He, Ne) $\gamma = \frac{f+2}{f} = \frac{5}{3} = \frac{c_p}{c_v}$

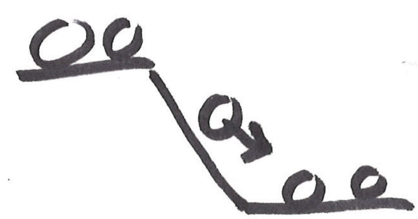
diatomic (N_2, O_2) (300K, f=5) $\frac{7}{5}$

<u>Only</u> isotherms and abiabats are reversible strokes.

Mechanical Analogy



Non-revers.



Efficiency

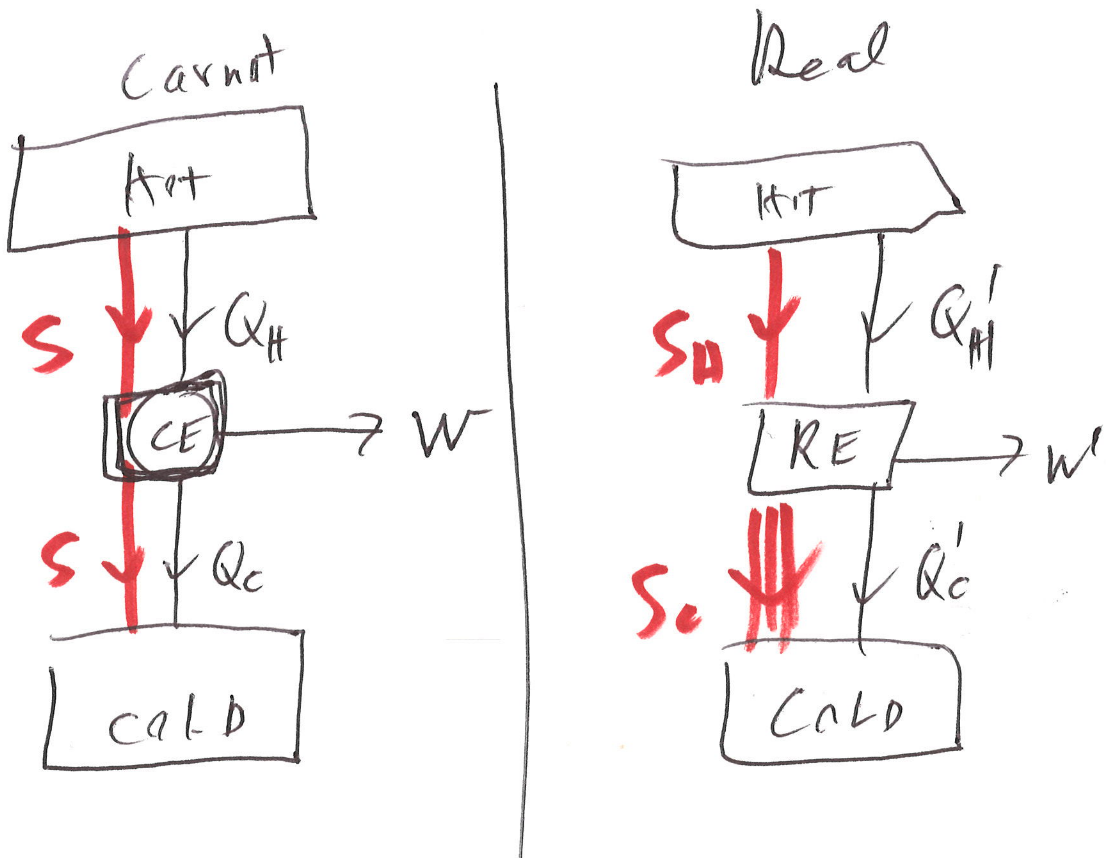
$$\eta_{real} = \frac{Q'_H - Q'_c}{Q'_H} < \eta_{carnot} = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H}$$

$$= 1 - \frac{T_c}{T_H}$$

for the Carnot Engine <u>only</u>: $\frac{Q_c}{T_c} = \frac{Q_H}{T_H}$

not the real engine.

$\frac{Q}{T}$ is conserved $\equiv S$



Heat Capacity: $C_{xy} = \left(\frac{\partial Q}{\partial T}\right)_{xy}$ ← path dependent.

1st Law: $dQ = dU + pdV - \mu dN$

hold N fixed

$$C_{VN} = \boxed{C_V = \left(\frac{\partial Q}{\partial T}\right)_{VN}} = \left(\frac{\partial U}{\partial T}\right)_{VN}$$

↑ extensive like Q, U

$$c_V = \frac{C_V}{\nu} = \text{specific heat}$$

↑ intensive

↖ "nu" = # of moles

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

For an ideal gas: $U = U(T)$ $\qquad pV = \nu RT$

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

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

$C_p - C_v = \nu R$ divide by ν

ideal gas

monatomic $f = 3$

diatomic $f = 5, 7$

$$\boxed{c_p - c_v = R}$$

$$C_v = \frac{f}{2}\nu R = \frac{f}{2} N k_B$$

$$\gamma \equiv \frac{c_p}{c_v} = \frac{f+2}{f}$$

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

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

ideal $\Rightarrow PV = \nu RT$ $\quad\boxed{dU = \nu c_v\, dT}$

adiabatic $\Rightarrow dQ = 0 \Rightarrow$ 1st Law $\boxed{dU = dW = -p\,dV}$

N = fixed

$PV = \nu RT$ take derivative both sides

$$p\,dV + V\,dp = \nu R\,dT = \cancel{\nu} R \frac{dU}{\cancel{\nu} c_v} = \frac{R}{c_v} dU$$

$$p\,dV + V\,dp = -\frac{R}{c_v} p\,dV$$

$R = c_p - c_v$

$$V\,dp = p\,dV\left(-1 - \frac{R}{c_v}\right) = -\left(\frac{c_p}{c_v}\right) p\,dV$$

$$= -\gamma\, p\,dV$$

$$\gamma\, p\,dV + V\,dp = 0$$ divide by PV

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0$$ integrate

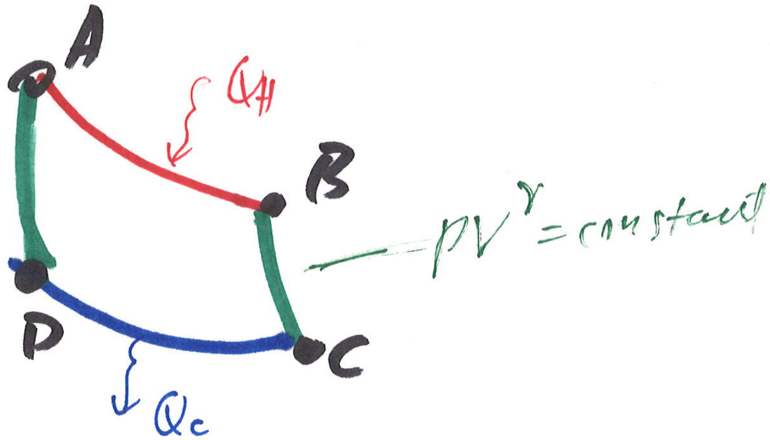
$$\gamma \ln(V) + \ln(P) = \text{constant}$$

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

exponentiate both sides $PV^\gamma = \text{constant}$

$R > 0$, $c_p > c_v \Rightarrow \gamma > 1$ adiabats steeper than isotherms

Back to the Carnot Cycle



Find Q_H $(T_H = \text{constant}) \Rightarrow$ $U(T) \Rightarrow dU = 0$

$đQ = -đW \Rightarrow Q_H = -W$

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

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

Look at adiabats $PV^\gamma = \text{const}$, $PV = \nu R T$

$$\frac{\nu R T}{V} V^\gamma = \text{constant} \Rightarrow T V^{\gamma - 1} = \text{const.}$$

$T_H V_B^{\gamma-1} = T_c V_c^{\gamma-1}$ — right adiabat

$T_H V_A^{\gamma-1} = T_c V_D^{\gamma-1}$ — left adiabat

divide LHS, RHS

$$\frac{\cancel{T_H} V_B^{\gamma-1}}{\cancel{T_H} V_A^{\gamma-1}} = \frac{\cancel{T_c} V_c^{\gamma-1}}{\cancel{T_c} V_D^{\gamma-1}} = \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_c}{V_D}\right)^{\gamma-1}$$

$$\Rightarrow \boxed{\frac{V_B}{V_A} = \frac{V_c}{V_D}}$$

$$Q_H = \nu R T_H \ln\left(\frac{V_B}{V_A}\right)$$

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

$$Q_c = \frac{T_c}{T_H} Q_H \Rightarrow \frac{Q_c}{Q_H} = \frac{T_c}{T_H}$$

Work done by Carnot Cycle

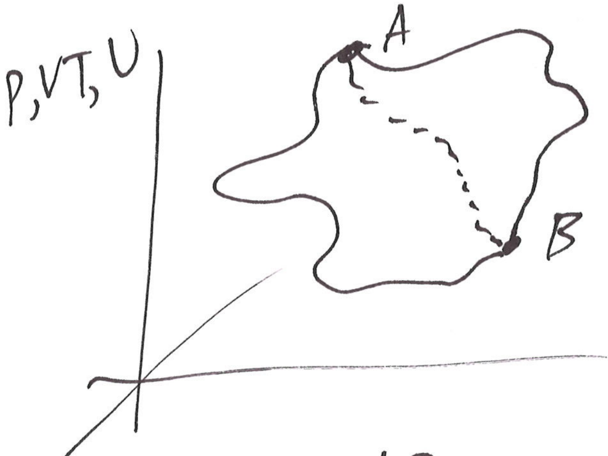
$$W = Q_H - Q_c \Rightarrow$$

$$\eta_c = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H} = \boxed{1 - \frac{T_c}{T_H}}$$

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$ mult by Q_H, divide by T_C

$$\Rightarrow \frac{Q_C}{T_C} = \frac{Q_H}{T_H} \equiv S$$

Clausius' Theorem



$$\boxed{\oint \frac{dQ_{reversible}}{T} = 0}$$

There is a state function $\equiv S$

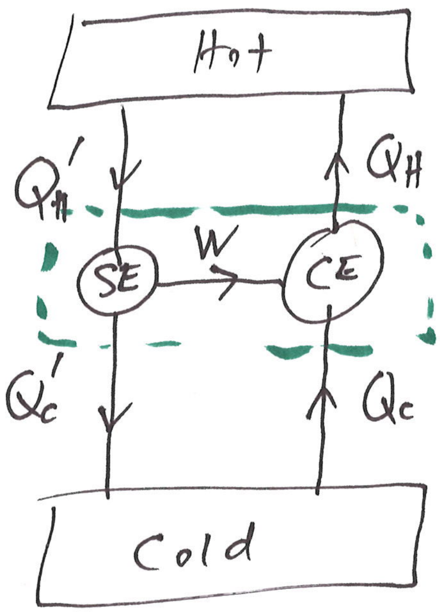
$$dS = \frac{dQ_{reversible}}{T}$$

$$\int_A^B \frac{dQ_{reversible}}{T} \equiv S_B - S_A = \Delta S$$

$$\oint \frac{dQ_{irreversible}}{T} \leq 0$$

Suppose $\exists$ A Super Engine (SE)

with $\eta_s > \eta_c = 1 - \frac{T_c}{T_H}$



1st Law $\quad W = Q_H' - Q_c'$

$$W = Q_H - Q_c$$

$$\eta_c = 1 - \frac{T_c}{T_H} < \eta_s = 1 - \frac{Q_c'}{Q_H'}$$

$$1 - \frac{Q_c}{Q_H} < 1 - \frac{Q_c'}{Q_H'}$$

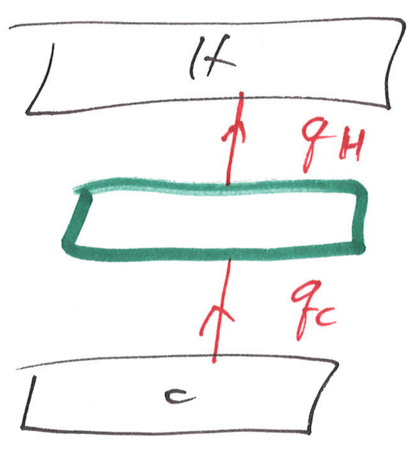
$$\frac{Q_H - Q_c}{Q_H} < \frac{Q_H' - Q_c'}{Q_H'}$$

$$\frac{W}{Q_H} < \frac{W}{Q_H'} \Rightarrow Q_H' < Q_H$$

$$Q_c' = Q_H' - W$$

$$Q_c = Q_H - W$$

$$\Rightarrow Q_c' < Q_c$$



$\bar{C}$

anti-Clausius machine

$$dS = \frac{dQ_{reversible}}{T} = \frac{dU - dW}{T} \quad (1^{st}\ \text{Law})$$

$$dW = -p\,dV_{gas}$$

$$dS = \frac{dU}{T} + p\frac{dV}{T}$$

ideal gas

$$U = \frac{f}{2}\nu RT$$

$$dU = \frac{f}{2}\nu R\,dT$$

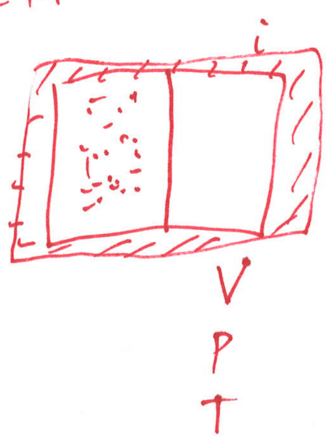
$$\frac{P}{T} = \frac{\nu R}{V}$$

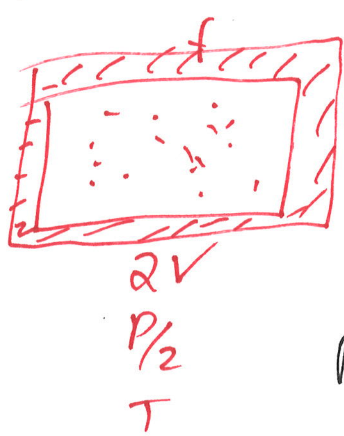
$$dS = \frac{\frac{f}{2}\nu R\,dT}{T} + \frac{\nu R\,dV}{V}$$

$$\int_i^f dS = \int_{T_i}^{T_f} \frac{\frac{f}{2}\nu R\,dT}{T} + \nu R\int_{V_i}^{V_f}\frac{dV}{V}$$

$$\Delta S = S_f - S_i = \frac{f}{2}\nu R\ln\left(\frac{T_f}{T_i}\right) + \nu R\ln\left(\frac{V_f}{V_i}\right)$$

Ex. Joule - Thomson (Kelvin) Expansion





$$\Delta S = \nu R\ln(2)$$