First Law $dU = \sum_i J_i \, d\xi_i + TdS + \sum_j \mu_j dN_j$

mechanical | thermal | chemical

spring $F\,dx$ (tension)

gas $(-P)dV$

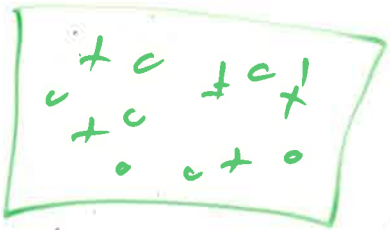
spring  mechanical equilibrium

same $F_{tension}$, trading x

gas 

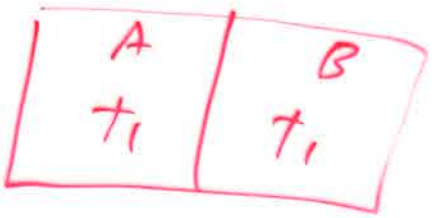
same pressure, trade volume V

chemical equilibrium



same μ (energy)
trading N (# of particles)

thermal equilibrium



same T, trade entropy

Third Law (Walther Nernst) 1906-12

→ It is impossible to reach 0K in a finite number steps.

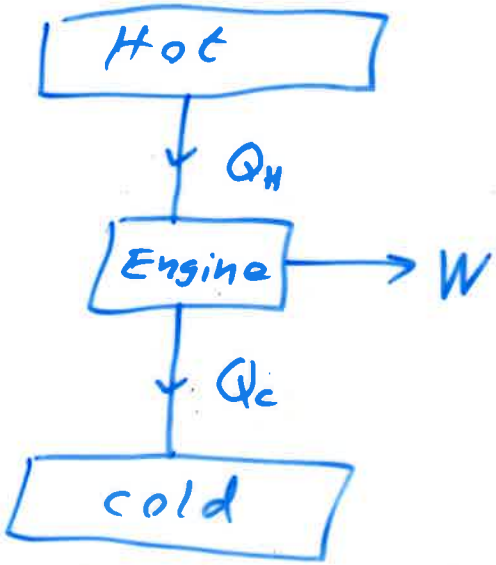
→ Heat capacity $C_p \to 0$ as $T \to 0K$

ideal gas (monatomic) $C_V = \frac{3}{2}nR$, $C_p = \frac{5}{2}nR$

$C_p \not\to 0$ as 0K (problem)

Second Law Sadi Carnot 1824

maximum theoretical efficiency of engines

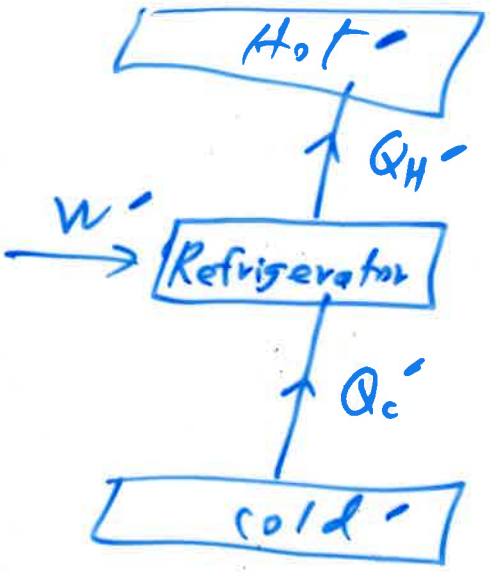


efficiency

$$\eta = \frac{W}{Q_H}$$

$$= \frac{Q_H - Q_c}{Q_H}$$

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



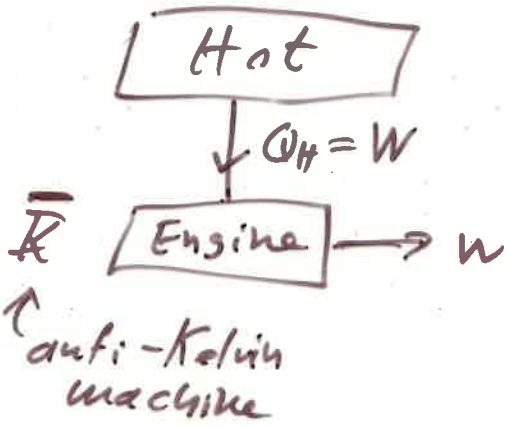
coefficient of performance

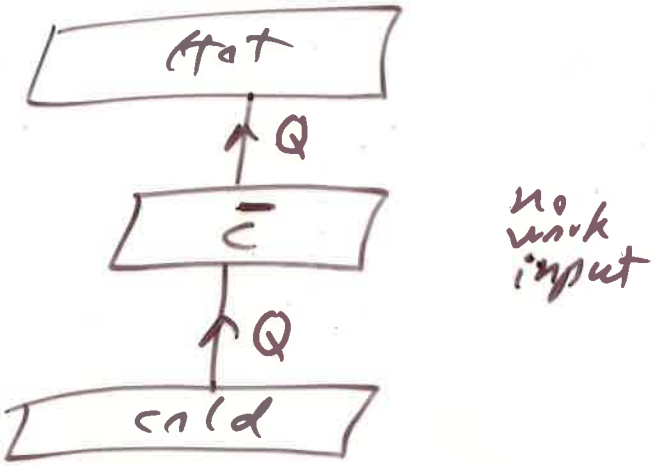
$$COP = \omega = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_c}$$

$\omega \geq 1$

$\omega > 1$

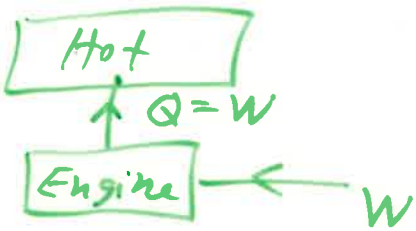
Kelvin (K): There is no perfect heat engine

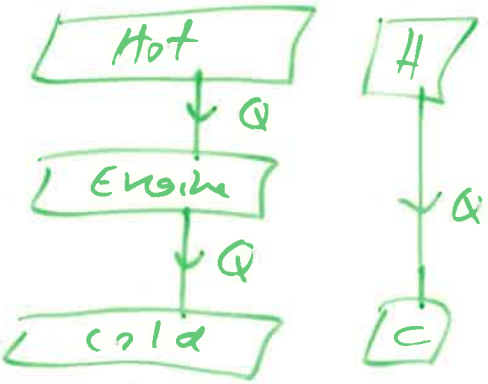




Clausius (C): There is no perfect refrigerator

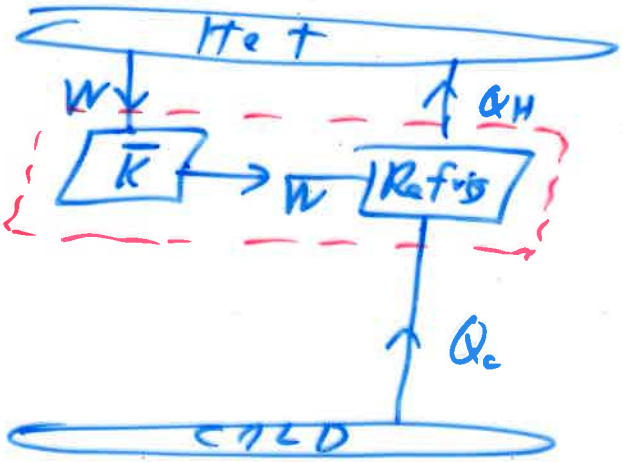
These are possible

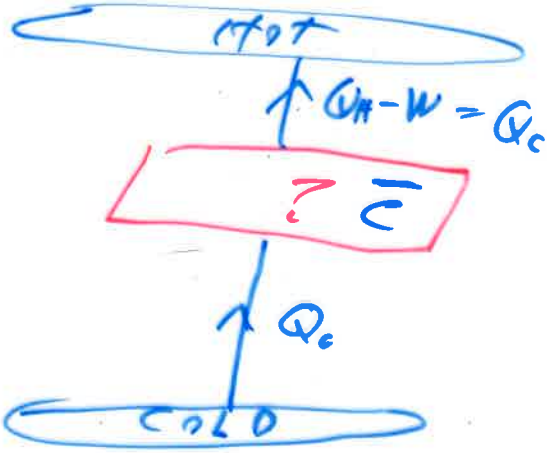


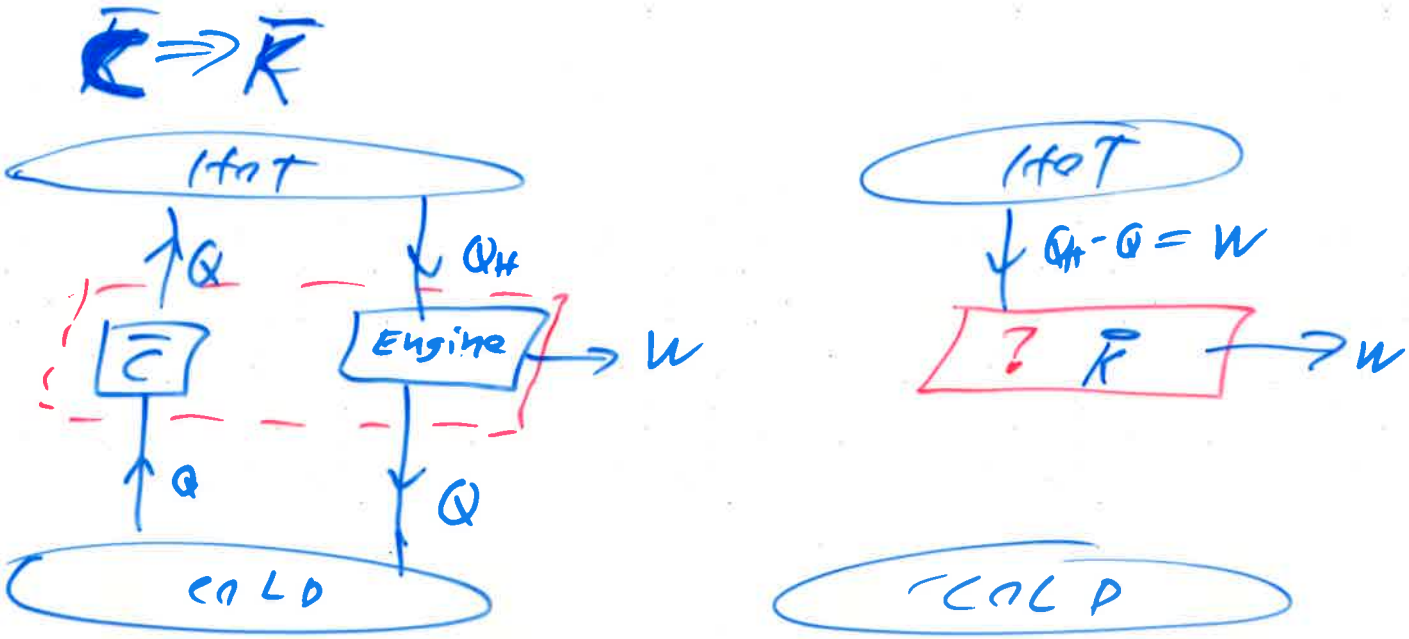


$\bar{K} \Leftrightarrow C$ $\quad \bar{K} \rightarrow \bar{C}$ and $\bar{C} \Rightarrow \bar{K}$

$\bar{K} \Rightarrow \bar{C}$



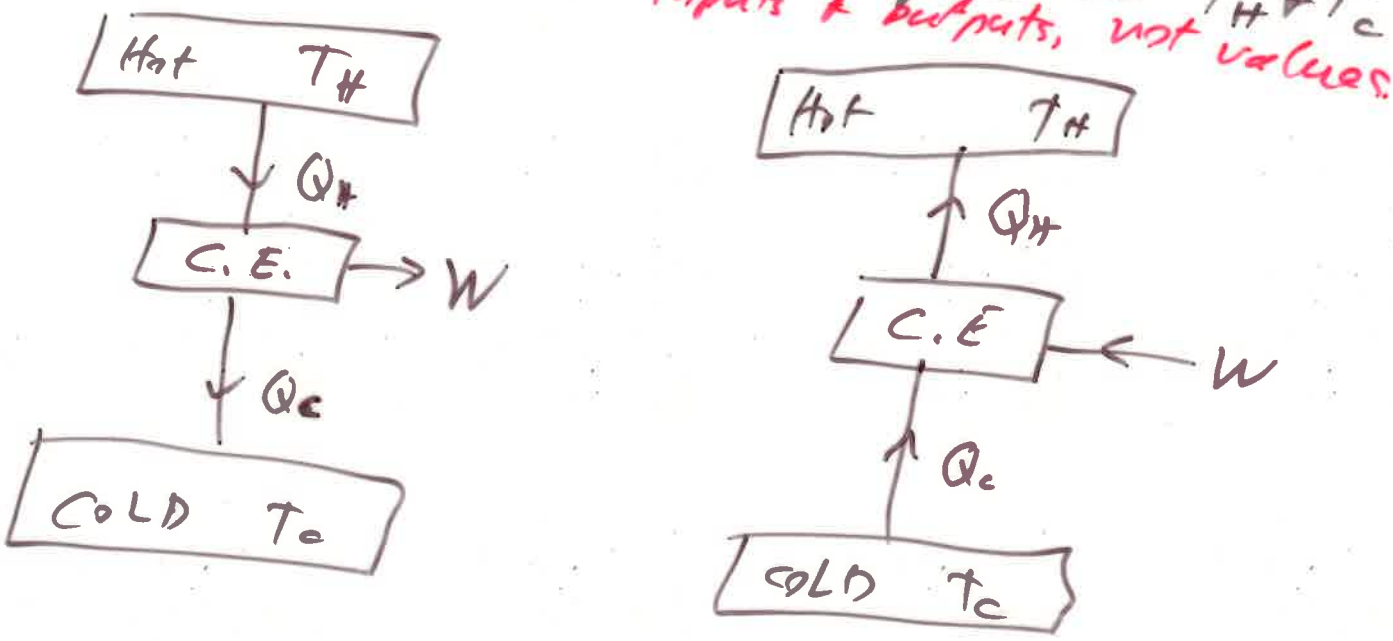




Carnot Engine (C.E.)

Reversible, cyclic, operates between two temperatures $T_H \neq T_C$

change the direction of inputs & outputs, not values



Carnot Engine concept is independent of the working substance. But look at an ideal gas.

Equation of State: $PV = NkT = nRT$

$n = \frac{N}{N_A}$, $k_B = \frac{R}{N_A}$

N: total # particles; n: # of moles