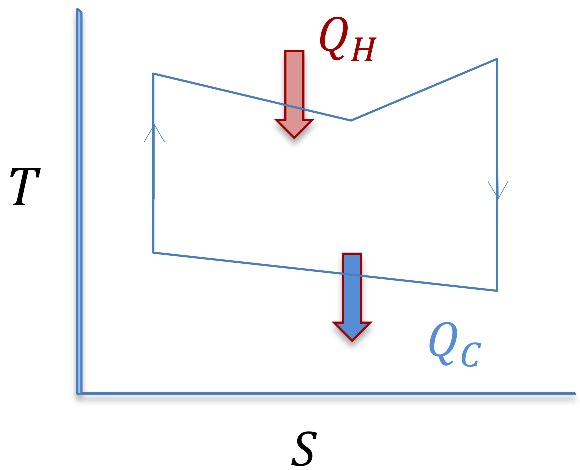
Notes for today

- Problem set for tomorrow, looking for volunteers for #3, 4, 5.
- Today finishing Ch. 4. Then: section 5.1 followed by chapter 6 (Free energies).
- Exam coming in 3 weeks: It will include the first part of chapter 6, precisely how far still to be determined. You can prepare a formula sheet (e.g. one regular-size page, both sides).

Cycles recall:



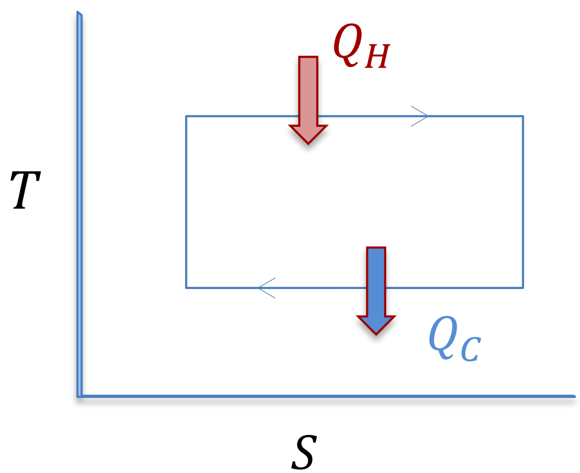
cycle run as heat engine:

$$W_{ext} = -\boxed{W_{system}} > 0$$

"W"

$$\varepsilon_e = \frac{W_{ext}}{Q_H} \quad \Leftarrow \quad \text{General case}$$

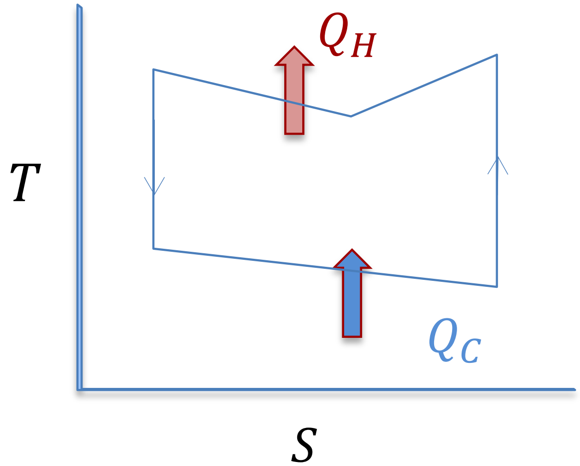
$$\varepsilon_e \leq 1 - \frac{T_C}{T_H} \quad \Leftarrow \quad \text{Maximum case} = \text{Carnot result}$$

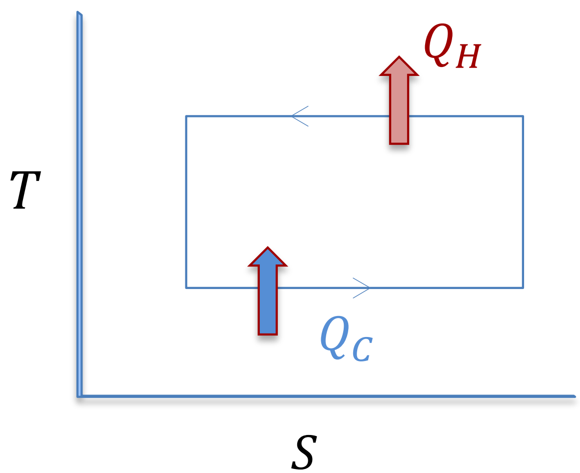


- Heat: Q_H & $Q_C > 0$ my notation used here (the magnitudes) e.g. problem 5.
- Entropy: $\Delta S = 0$ (means the *system*). But $\Delta S_{universe} \geq 0$ no matter what direction the cycle operates.

Cycles recall:

refrigerator





cycle run as refrigerator
(or heat pump):

$$W_{ext} = -W_{system} < 0$$

"W"

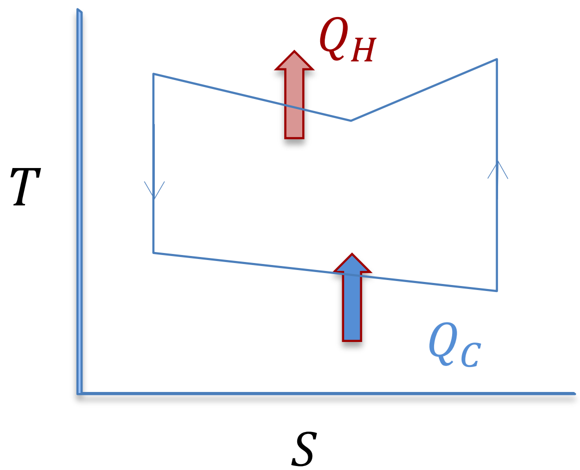
Q_H & $Q_C > 0$:
So $W_{ext} = -Q_H + Q_C$ 1st law

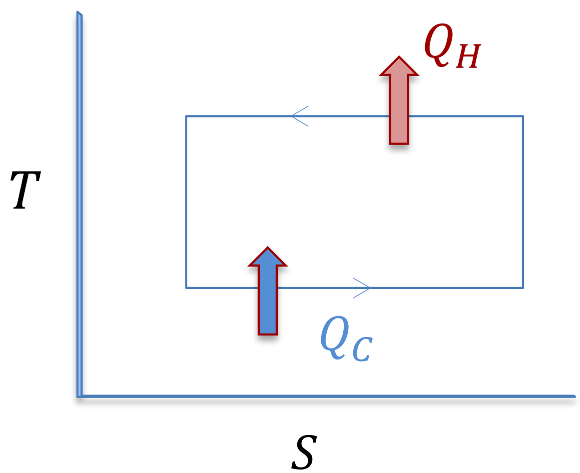
$$\varepsilon_R = \frac{Q_C}{-W_{ext}}$$ ⇦ Refrigerator COP

$$\varepsilon_R \leq \frac{T_C}{T_H - T_C}$$ ⇦ Maximum case = Carnot result

Cycles recall:

refrigerator





cycle run as refrigerator
(or heat pump):

$$\varepsilon_R = \frac{Q_C}{-W_{ext}}$$ ⇦ Refrigerator COP

$$\varepsilon_R \le \frac{T_C}{T_H - T_C}$$ ⇦ Maximum case = Carnot result

Interesting results:

- COP can be >1
- Most efficient with ΔT small not large.
- Careful about arrows! Heat flows from hot to cold.

Maximum work theorem:

- Applies for *one-reservoir* problems
- Consider that system can perform work on external "reversible work system", W_{ext}. [Reversible means *no friction*; otherwise this is ordinary work as we have seen, idealized work we have been considering is reversible.]
- Question, what is maximum W_{ext} possible if a system goes from state 1 to state 2?
- Find: $W_{ext} \leq -\Delta U + T_{res}\Delta S$
- Maximum is <u>reversible</u> path from 1 to 2.

Maximum work theorem:

- Applies for *one-reservoir* problems
- Consider that system can perform work on external "reversible work system", W_{ext}. [Reversible means *no friction*; otherwise this is ordinary work as we have seen, idealized work we have been considering is reversible.]
- Question, what is maximum W_{ext} possible if a system goes from state 1 to state 2?
- Find: $W_{ext} \leq -\Delta U + T_{res}\Delta S$

$$\Delta U = U_2 - U_1$$

system

$$\Delta S = S_2 - S_1$$

reversible path means
universe, not system.

Maximum work theorem:

- Applies for *one-reservoir* problems [consider first cold reservoir, $Q_{res} > 0$ "heat into reservoir"; $\Delta S < 0.$]

  Ideal gas example:
  - Isothermal, $Q_{res} = -W_{ext}.$
    ΔS & ΔS_{res} differ if non-equivalent T.
  - Adiabatic, $\Delta U = -W_{ext}$

$$\Delta U = U_2 - U_1$$

system

$$\Delta S = S_2 - S_1$$

reversible path means
universe, not system.

Maximum work theorem:

- Applies for *one-reservoir* problems [consider first cold reservoir, $Q_{res} > 0$ "heat into reservoir"; $\Delta S < 0$.]

  Ideal gas example:
  - Isothermal, $Q_{res} = -W_{ext}$.
    ΔS & ΔS_{res} differ if non-equivalent T.
  - Adiabatic, $\Delta U = -W_{ext}$
  - Can combine these, easy to see $W_{ext} = -\Delta U + T_{res}\Delta S$

$$\Delta U = U_2 - U_1$$

$$\Delta S = S_2 - S_1$$

system

reversible path means
<u>universe</u>, not system.

Maximum work theorem:

General proof: combine 1st law and 2nd law.

$$dU + dQ_{res} + dW_{res} = 0$$

I omitted bars on $dQ_{res} + dW_{res}$, they belong there

$$dS_{tot} = dS + dQ_{res}/T_{res} \geq 0$$

$$\Delta U = U_2 - U_1$$

system

$$\Delta S = S_2 - S_1$$

Maximum work theorem:

General proof: combine 1st law and 2nd law.

$$dU + dQ_{res} + dW_{ext} = 0$$

I omitted bars on $dQ_{res} + dW_{res}$, they belong there

$$dS_{tot} = dS + dQ_{res}/T_{res} \geq 0$$

$$\Rightarrow dW_{ext} \leq -dU + T_{res}dS$$

or

$$W_{ext} \leq -\Delta U + T_{res}\Delta S$$

Result is very general; applies for reservoir of either sign (e.g. hot or cold, not both)
2nd term is "second law penalty", means all internal energy not necessarily available.

Maximum work theorem:

$$\Rightarrow dW_{ext} \leq -dU + T_{res} dS$$

or

$$W_{ext} \leq -\Delta U + T_{res} \Delta S$$

Result is very general; applies for reservoir of either sign (e.g. hot or cold, not both)
2nd term is "second law penalty", means all internal energy not necessarily available.

Examples:
Efficiency to generate electrical energy by cooling a fluid or a gas?
Convert electrical to mechanical energy?