This is not a replacement for your textbook. It is essential to study from your textbook!

Objectives

Ch 20: Entropy and the second law of thermodynamics

20-1 Entropy

20-2 Entropy in the real world: engines

20-3 Entropy in the real world: refrigerators.

~~20-4~~

20-1 Entropy

possible process	50°C	30°C	$\xrightarrow{\text{wait}}$	40°C	40°C
impossible process	40°C	40°C	$\xrightarrow{\text{wait}}$	50°C	30°C

energy is conserved

In an isolated system, for a process to occur, the entropy S of the system must not decrease.

$$\boxed{\text{Closed system,} \quad \Delta S \geq 0}$$

For a reversible process

$$\Delta S = \int_i^f \frac{dQ}{T}$$

final state

Heat transferred to the system

Change in entropy

initial state

temperature in Kelvins

If the change in temperature ΔT is much smaller than the initial and final temperature

$$\Delta S \approx \frac{1}{T_{avg}} \int_i^f dQ = \frac{Q}{T_{avg}} \qquad \text{for } \Delta T \ll T_{avg}$$

1 kg water

$$\boxed{20^\circ C} \rightarrow \boxed{30^\circ C}$$

$\Delta T = 10\ K$

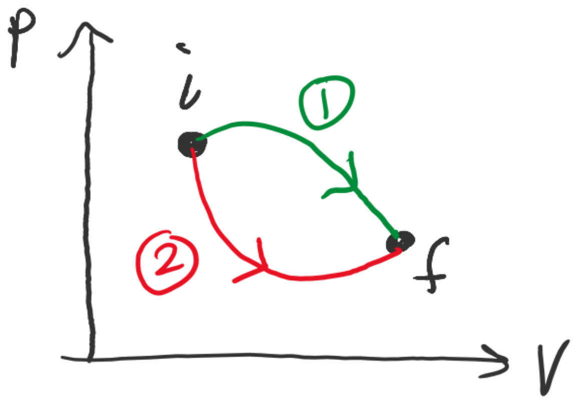
$T_{avg} = 25 + 273\ K$

$T_{avg} = 298\ K \gg \Delta T$

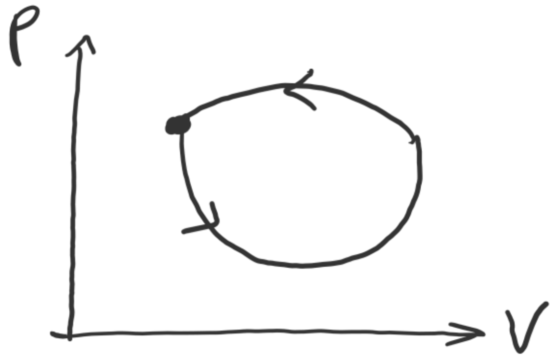
$$\Delta S \approx \frac{Q}{T_{avg}} = \frac{m c_w \Delta T}{T}$$

Entropy is a state property.

ΔS does not depend on path.



$\Delta S_1 = \Delta S_2$



$\Delta S = 0$

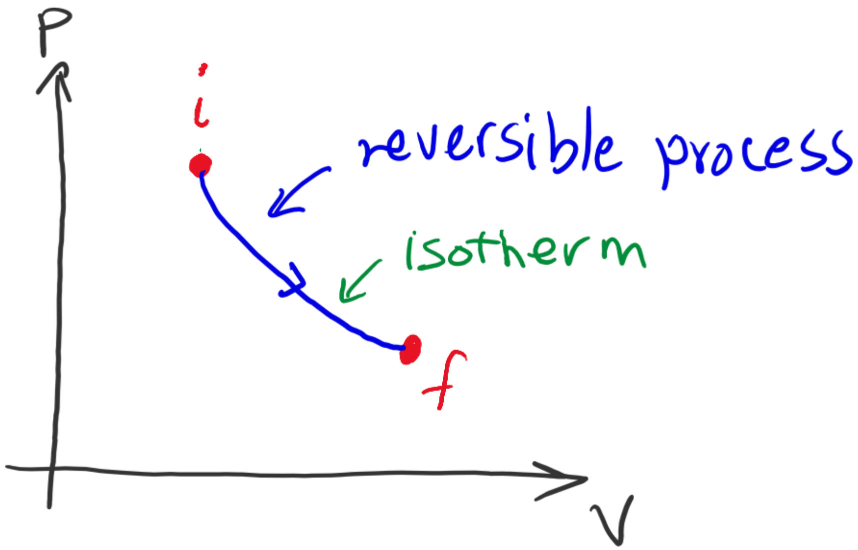
$S_{initial} = S_{final}$

For a reversible process, $\Delta S \equiv \int_i^f \frac{dQ}{T}$

How to find ΔS for irreversible process?

Since ΔS does not depend on path,
connect the initial and final states with a reversible process
and use $\Delta S = \int \frac{dQ}{T}$

Free expansion
$T_i = T_f$



Ideal gas

$$\Delta E_{int} = Q - W \xrightarrow[\text{change}]{\text{small}} dE_{int} = dQ - p\,dV$$

$$\Delta E_{int} = n C_V \Delta T$$

$$pV = nRT \longrightarrow p = \frac{nRT}{V}$$

$$\Delta S = \int \frac{dQ}{T} = \int \frac{dE_{int} + p\,dV}{T} = \int \frac{n C_V dT}{T} + \int \frac{nR\,dV}{V}$$

$$\boxed{\Delta S = n C_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}}$$

Solid or Liquid

change T, same phase $\longrightarrow$ $\Delta S = \int \frac{mc\,dT}{T}$

$$\boxed{\Delta S = mc \ln \frac{T_f}{T_i}}$$

same T, change phase $\longrightarrow$ $\Delta S = \frac{Q}{T}$

$$\boxed{\Delta S = \frac{Lm}{T}}$$

Second law of thermodynamics

In a closed system, $\Delta S \geq 0$

change in entropy for the whole system

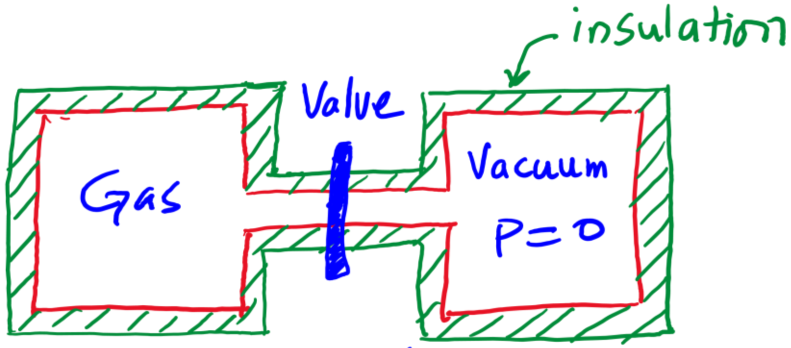
$\Delta S = 0$ for a reversible process

$\Delta S > 0$ for an irreversible process

In the real world, almost all processes are irreversible.

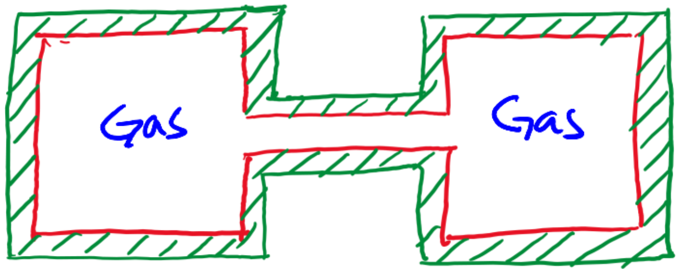
Example

Free expansion



initial

One mole



Final

$V_f = 2V_i$

Free expansion $T_f = T_i$

$\ln 1 = 0$

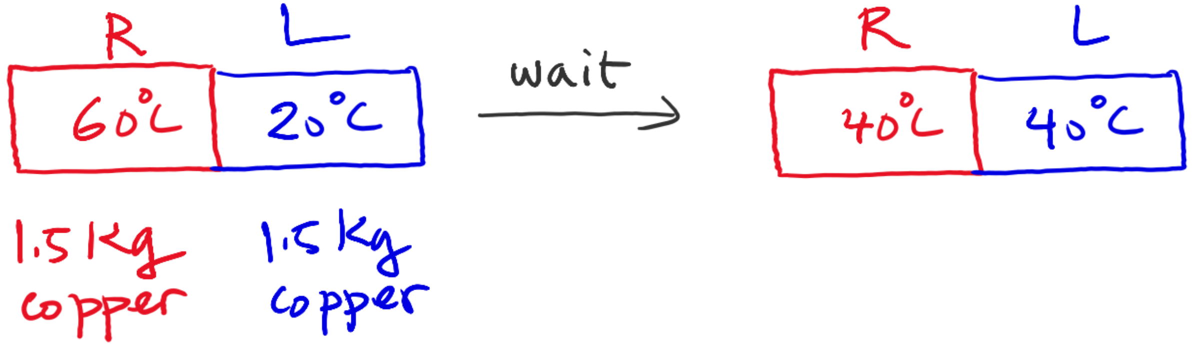
Change in entropy

$$\Delta S = \cancel{n C_v \ln \frac{T_f}{T_i}}^{\,0} + nR \ln \frac{V_f}{V_i} = (1)(8.31) \ln 2$$

$$= 5.8 \text{ J/K}$$

Example

Insulated system



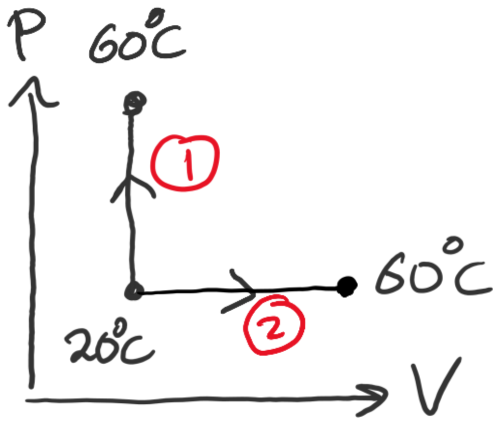
$$\Delta S_R = mc \ln \frac{T_f}{T_i} = (1.5)(386) \ln \frac{40+273}{60+273} = -36 \, J/K$$

$$\Delta S_L = mc \ln \frac{T_f}{T_i} = (1.5)(386) \ln \frac{40+273}{20+273} = 38 \, J/K$$

$$\Delta S = \Delta S_L + \Delta S_R = 2 \, J/K > 0$$

Question

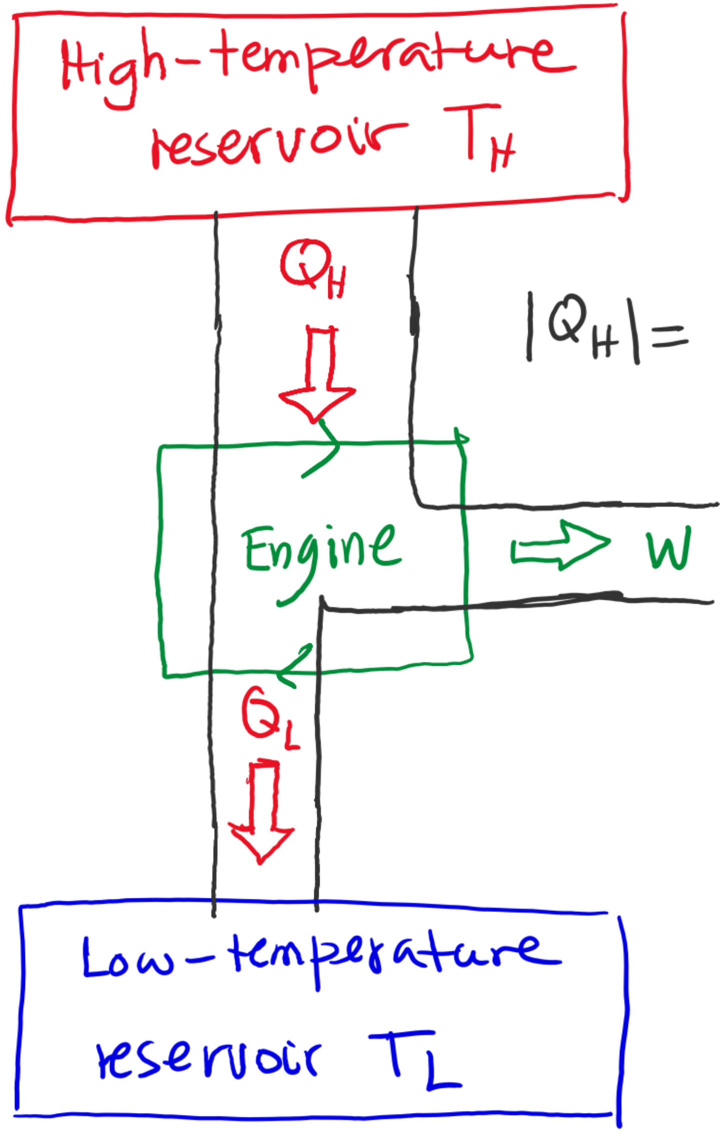
Compare ΔS_1 and ΔS_2



$$\Delta S = \underbrace{n C_v \ln \frac{T_f}{T_i}}_{\text{same for (1) and (2)}} + \underbrace{n R \ln \frac{V_f}{V_i}}_{\substack{\text{for (1)} = 0 \\ \text{for (2)} > 0}}$$

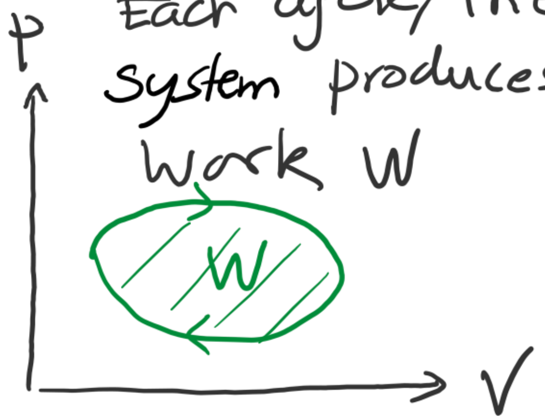
$$\Delta S_2 > \Delta S_1$$

20-2 Heat engines: Convert some heat to work video



$$|Q_H| = W + |Q_L|$$

Each cycle, the system produces work W



Ideal engine:

All processes are reversible

Carnot engine:

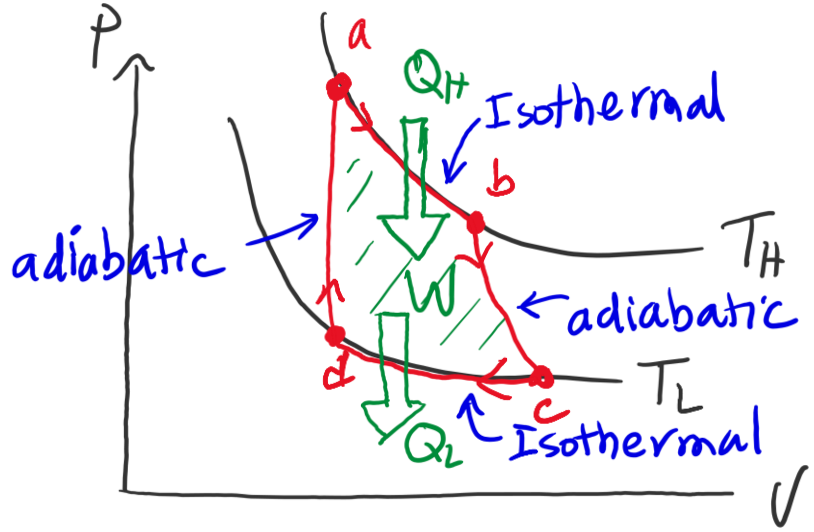
→ Ideal engine

→ working substane: ideal gas

→ most efficient engine

You cannot build more efficient engine than a Carnot engine.

Carnot engine



stroke a → b isothermal : $Q_H = W_{ab} > 0$

stroke b → c adiabatic : $Q = 0$

stroke c → d isothermal : $Q_L = W_{cd} < 0$

stroke c → a adiabatic : $Q = 0$

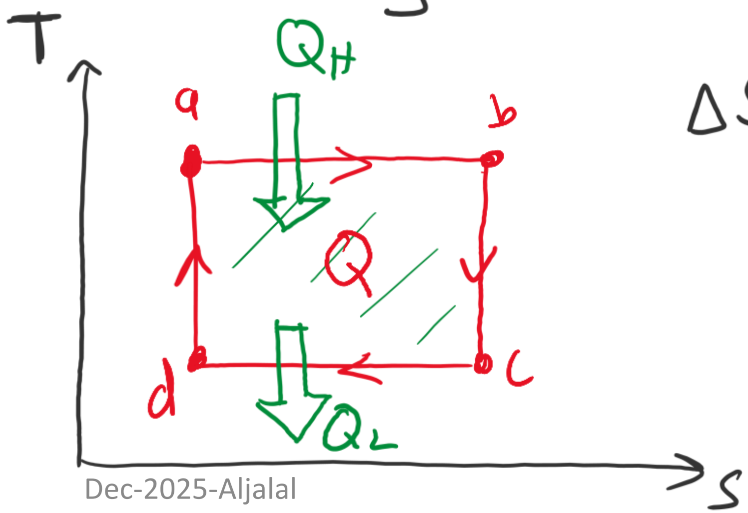
$$\Delta E_{int} = Q - W$$

0 cycle

$$W = Q = Q_H + Q_L$$

$$\boxed{W = |Q_H| - |Q_L|}$$

T-S diagram



$$\Delta S_{ab} = \frac{Q_H}{T}$$

$$\Delta S_{cd} = \frac{Q_L}{T} = -\frac{|Q_L|}{T}$$

0 cycle

$$\Delta S = \Delta S_{ab} + \Delta S_{cd} = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

$$\boxed{\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}}$$

Thermal efficiency of an engine

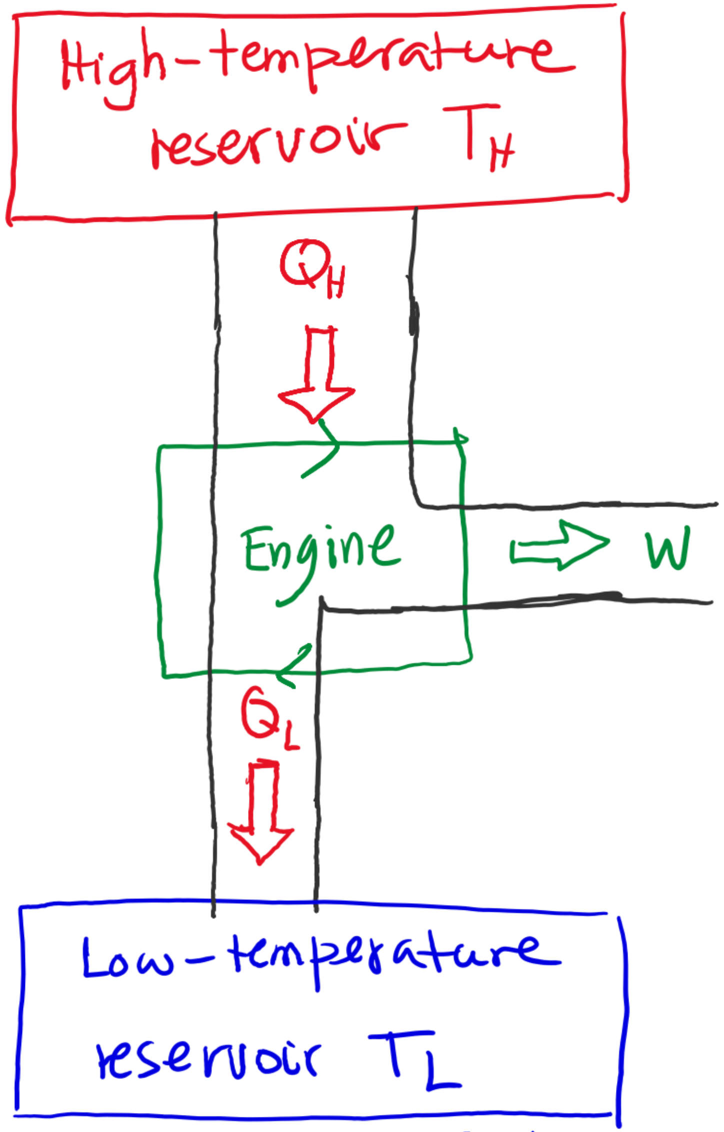
$$\varepsilon = \frac{\text{what you want}}{\text{what you pay}} = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_c|}{|Q_H|} = 1 - \frac{|Q_c|}{|Q_H|}$$

Thermal efficiency of a Carnot engine

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

$$\varepsilon_c = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

No real heat engine can have greater efficiency than ε_c



$$\varepsilon = 1 - \frac{|Q_c|}{|Q_H|}$$

$$\varepsilon_c = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

No real heat engine can have greater efficiency than ε_c

Closed system: Engine + two reservoirs

$$\Delta S_{system} = \Delta S_{gas} + \Delta S_{H\text{-}Res} + \Delta S_{L\text{-}Res}$$

$$\Delta S_{system} = 0 - \frac{|Q_H|}{T_H} + \frac{|Q_L|}{T_L} \geq 0$$

$$\frac{|Q_L|}{T_L} \geq \frac{|Q_H|}{T_H}$$

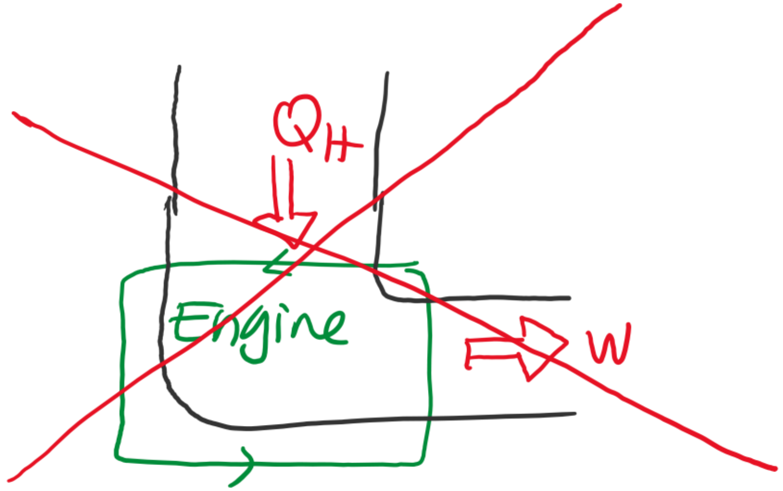
$$\frac{|Q_L|}{|Q_H|} \geq \frac{T_L}{T_H}$$

$$1 - \frac{|Q_L|}{|Q_H|} \leq 1 - \frac{T_L}{T_H} = \varepsilon_c$$

$$\varepsilon_c = 1 - \frac{T_L}{T_H}$$

$\varepsilon_c = 1$ if $T_L = 0$ or $T_H = \infty$ (impossible)

You cannot transfer heat completely to work.

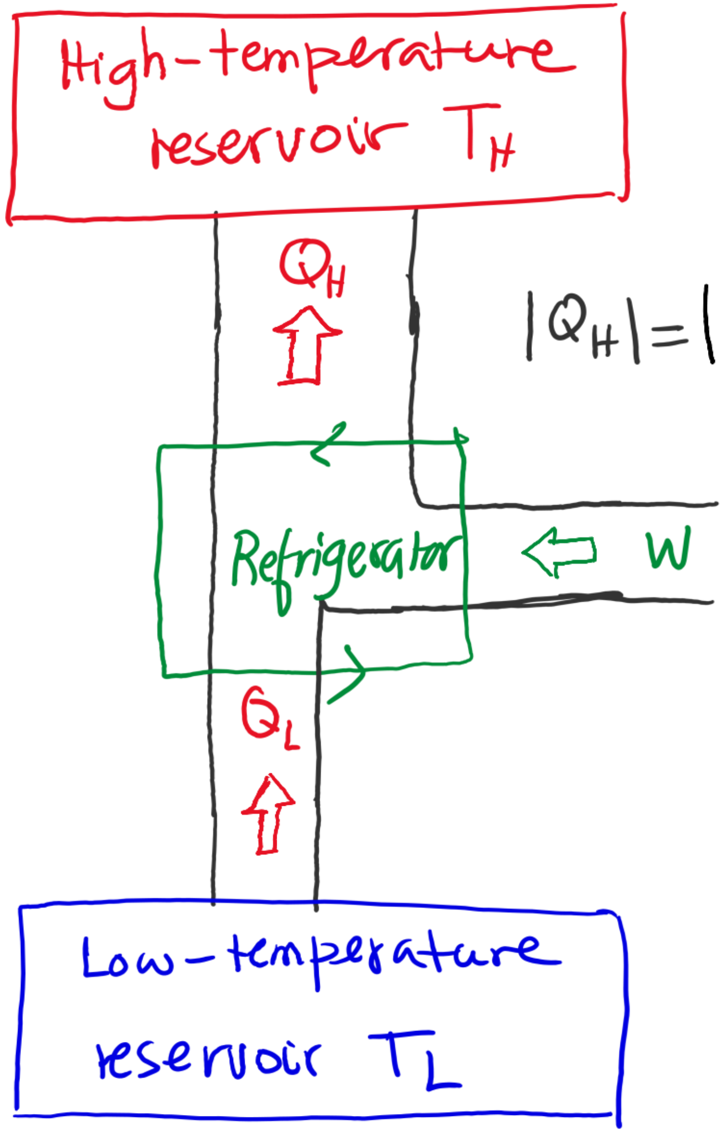


perfect engine

Always, you must have some heat wasted

Another form of the second Law You cannot build a <u>perfect</u> engine

20-3 Refrigerator



$$|Q_H| = |W| + |Q_L|$$

$$Q_L > 0$$
$$Q_H < 0$$
$$W < 0$$

Coefficient of performance

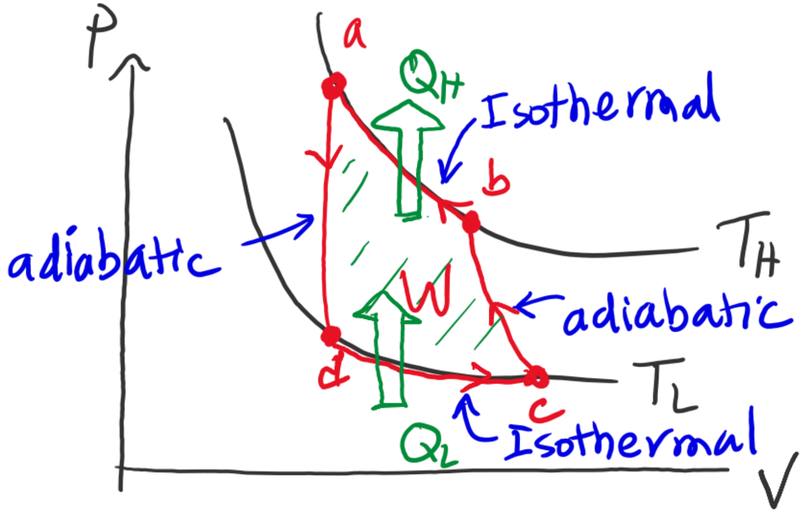
$$K = \frac{\text{what you want}}{\text{what you pay}} = \frac{|Q_L|}{|W|}$$

Air conditioner $K \approx 2.5$

$$|Q_H| = |W| + |Q_L| \qquad K = \frac{|Q_L|}{|W|}$$

Carnot Refrigerator

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L} \Rightarrow K_C = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{T_L}{T_H - T_L}$$



No perfect refrigerator

For a perfect refrigerator $|Q_H| = |Q_L| = |Q|$

Closed system: refrigerator + two reservoirs

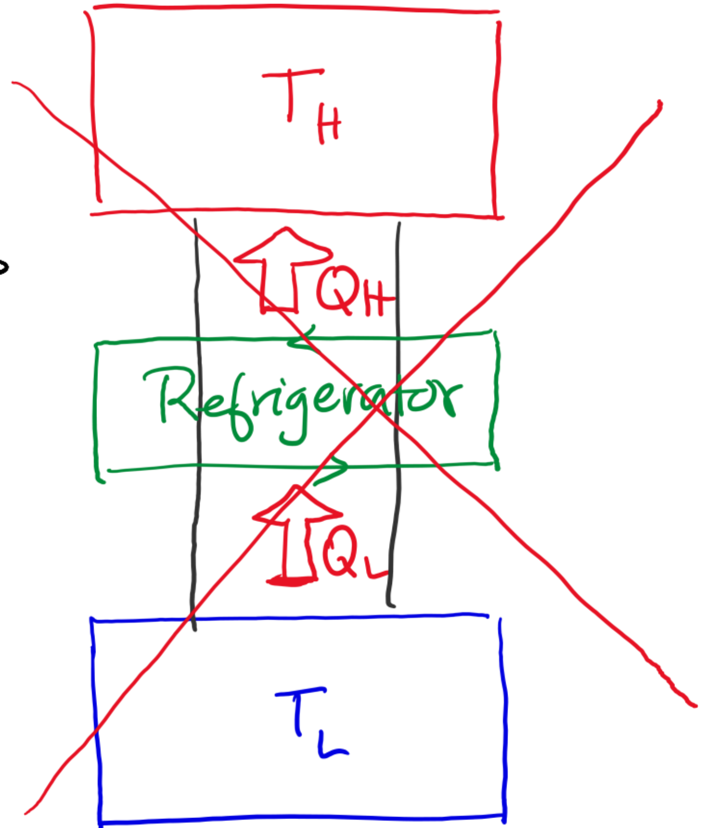
$$\Delta S_{\text{system}} = \Delta S_{\text{gas}} + \Delta S_{\text{H-Res}} + \Delta S_{\text{L-Res}}$$

$$\Delta S_{\text{system}} = 0 + \frac{|Q|}{T_H} - \frac{|Q|}{T_L}$$

$$\Delta S_{\text{system}} = |Q|\left(\frac{1}{T_H} - \frac{1}{T_L}\right) < 0$$

Violates the second law

bigger



perfect refrigerator

You must do work to move heat from Low-temperature to high-temperature reservoir

Another form of the second law

You cannot build a perfect refrigerator

Example

<u>Carnot engine</u>

$T_H = 600\ K$ $\quad$ $W = 500\ J$ per cycle

$T_L = 300\ K$ $\quad$ Each cycle takes $0.1\ s$

Efficiency: $\varepsilon_c = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{600} = 0.5 = 50\%$

Average power: $P = \frac{W}{t} = \frac{500}{0.1} = 5\ kW$

Heat extracted from the high-temperature reservoir:

$$\varepsilon_c = \frac{|W|}{|Q_H|} \Rightarrow |Q_H| = \frac{|W|}{\varepsilon_c} = \frac{500}{0.5} = 1000\ J$$

Heat delivered to the low-temperature reservoir:

$$|Q_L| = |Q_H| - W = 1000 - 500 = 500\ J$$

Question

Is it possible for a heat engine operated between $0^\circ C$ and $100^\circ C$ to have an effeciency of 75%?

$$\varepsilon_c = 1 - \frac{T_L}{T_H} = 1 - \frac{0+273}{100+273} = 0.27 = 27\%$$

Not possible.

Question Compare coefficient of performance

$$K = \frac{T_L}{T_H - T_L}$$

room temperature

refrigerator

T_H | $T_L + dT$

$$K = \frac{T_L + dT}{T_H - (T_L + dT)} \quad 1$$

$T_H + dT$ | T_L

$$K = \frac{T_L}{T_H + dT - T_L} \quad 3$$

T_H | $T_L - dT$

$$K = \frac{T_L - dT}{T_H - (T_L - dT)} \quad 4$$

$T_H - dT$ | T_L

$$K = \frac{T_L}{T_H - dT - T_L} \quad 2$$