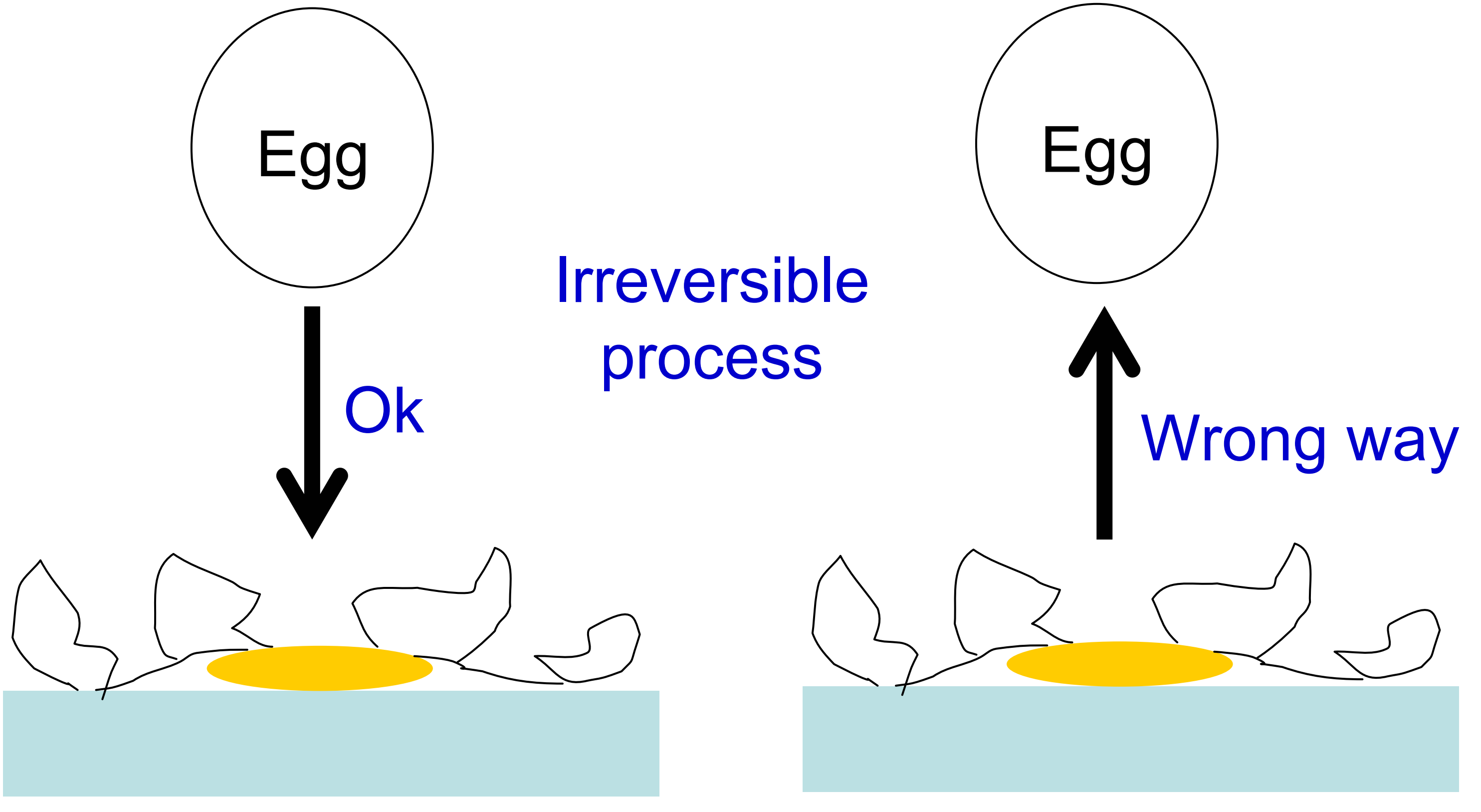
Chapter 21

Entropy
and
the Second Law of Thermodynamics

21-1 Some One-Way Processes

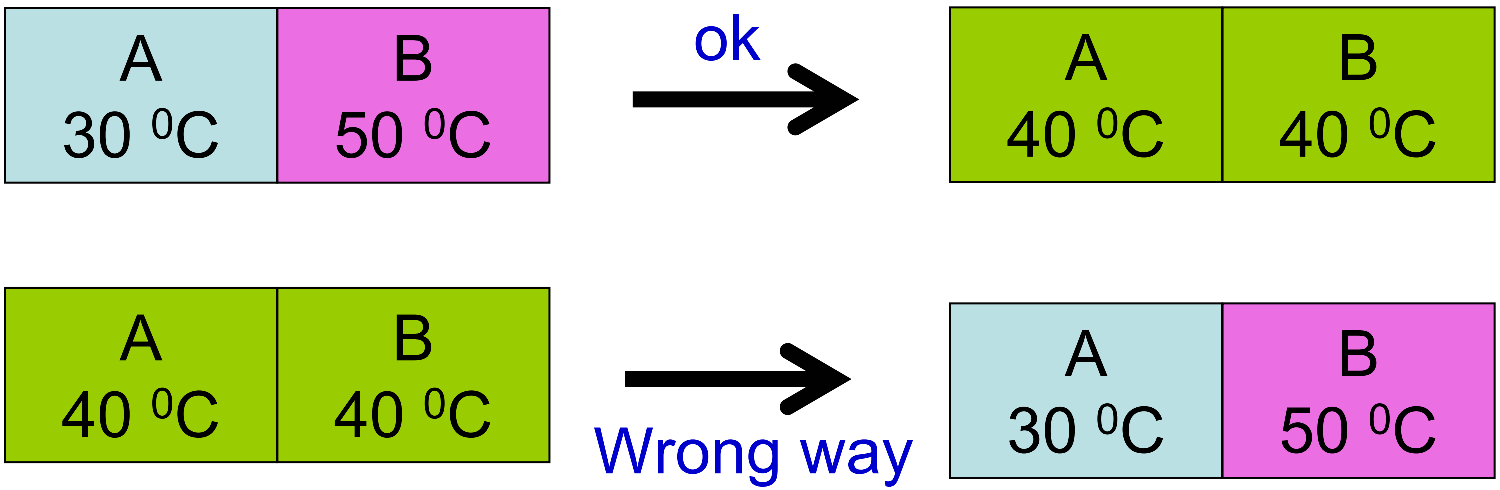


Why not?

Does not violate conservation of energy!

21-1 Some One-Way Processes

Irreversible
process



Why not?

Does not violate conservation of energy

21-1 Some One-Way Processes

The direction of the process is setup by a property called entropy S

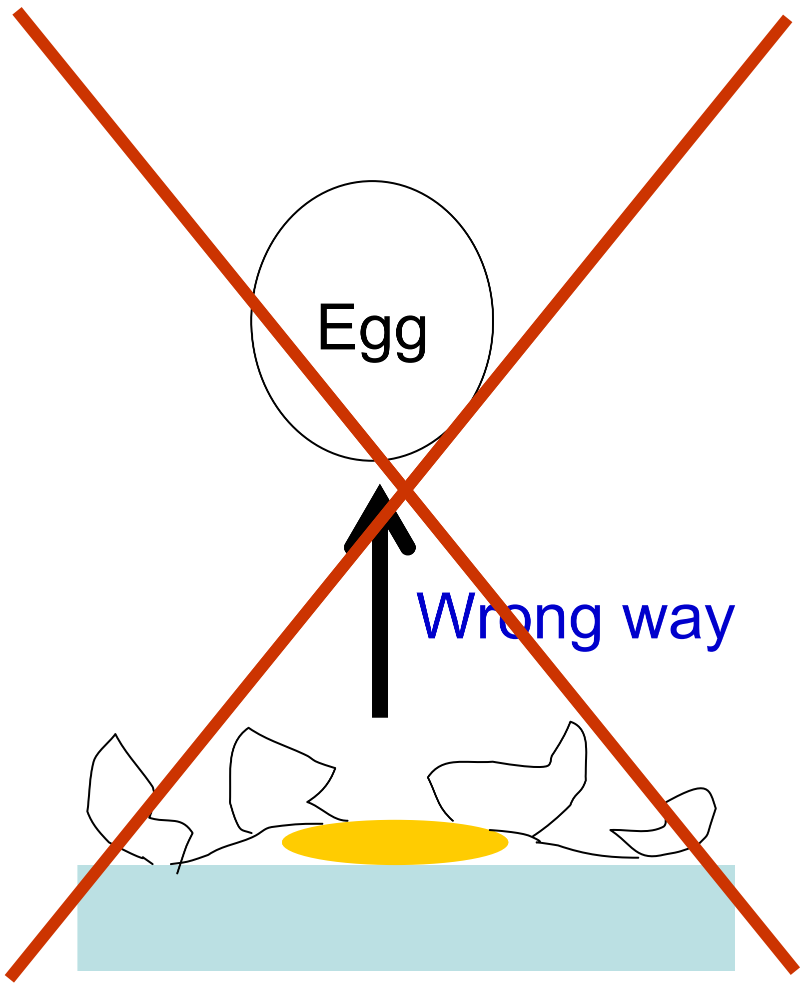
If an irreversible process occurs in a closed system, the entropy S of the system always increases, it never decreases.

Some times, the change in entropy is called “the arrow of time”

21-1 Some One-Way Processes

Entropy decreases

Process does not occur



21-2 Change in Entropy

Final state

Heat transfer to the system

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

For reversible processes

Change in entropy

Initial state

Temperature In kelvins

Entropy is measured in J/K

21-2 Change in Entropy

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

For reversible processes

If the change in temperature (in kelvins) is small compared to the heat transferred to the system

$$\Delta S = \int_i^f \frac{dQ}{T} \approx \frac{1}{T_{avg}} \int_i^f dQ$$

$$\Delta S \approx \frac{Q}{T_{avg}}$$

Average temperature

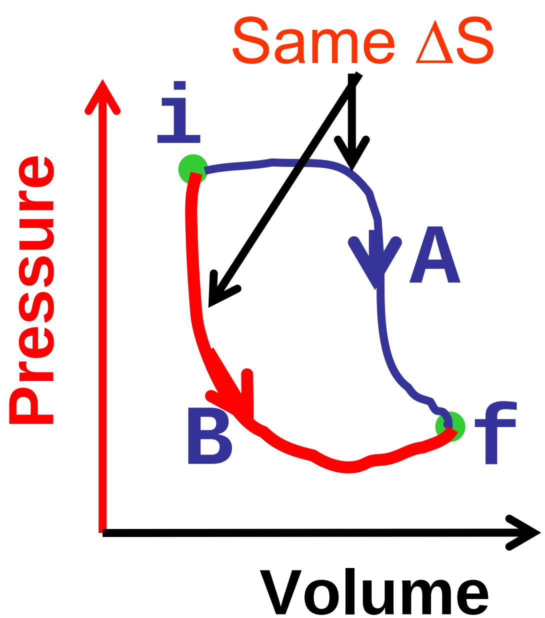
21-2 Change in Entropy

Checkpoint 1

21-2 Change in Entropy

Entropy is a state property.

The change in entropy between state i and f depends only on these states and not on the way the system takes from one state to the other.



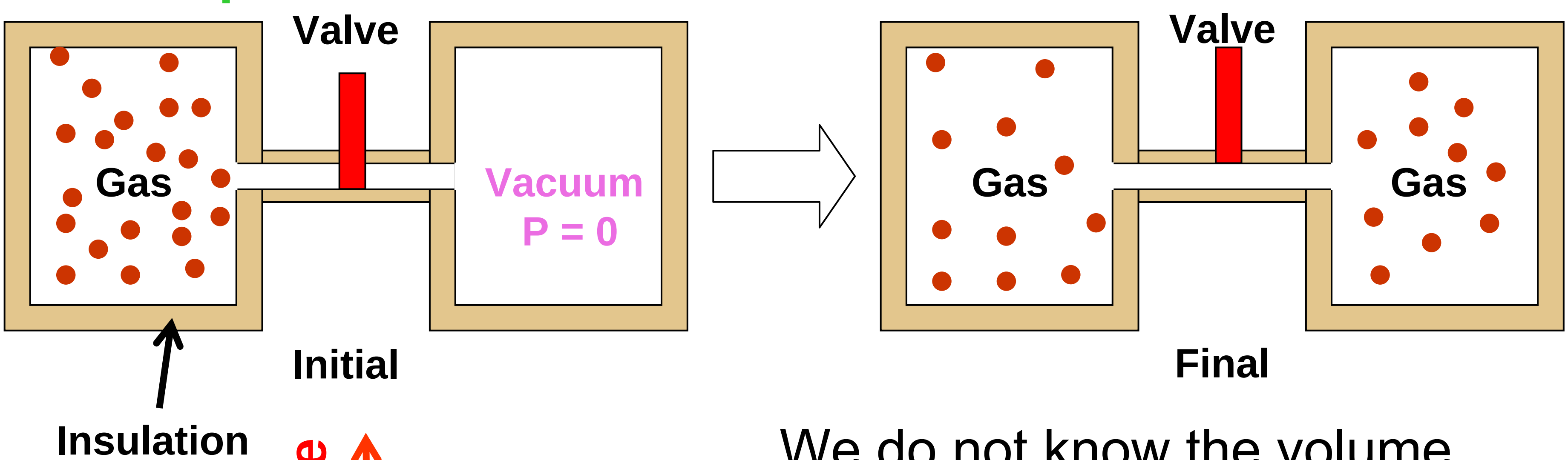
State properties:
Pressure
Volume
Temperature
Internal energy
Entropy

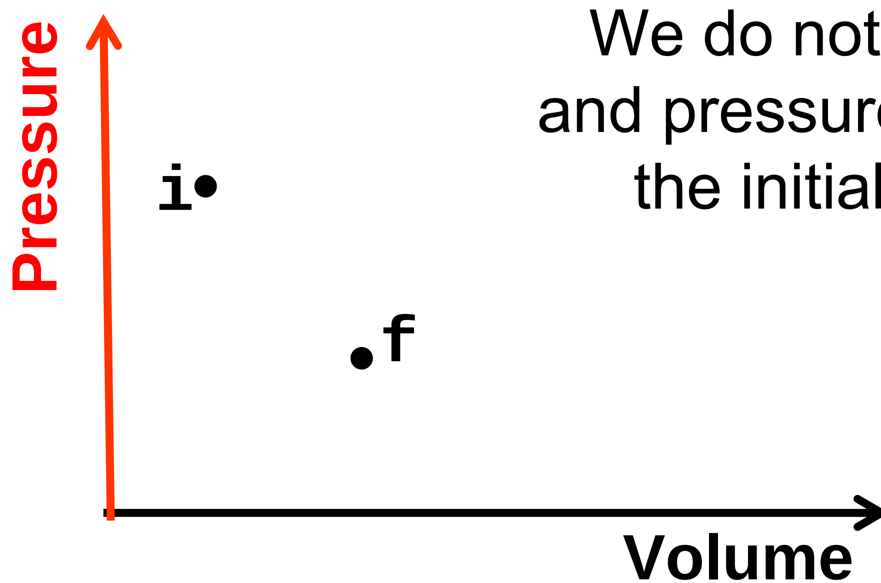
Work and heat are not state properties. They depend on the path

21-2 Change in Entropy

Example: The change in entropy of a free expansion process

Free expansion



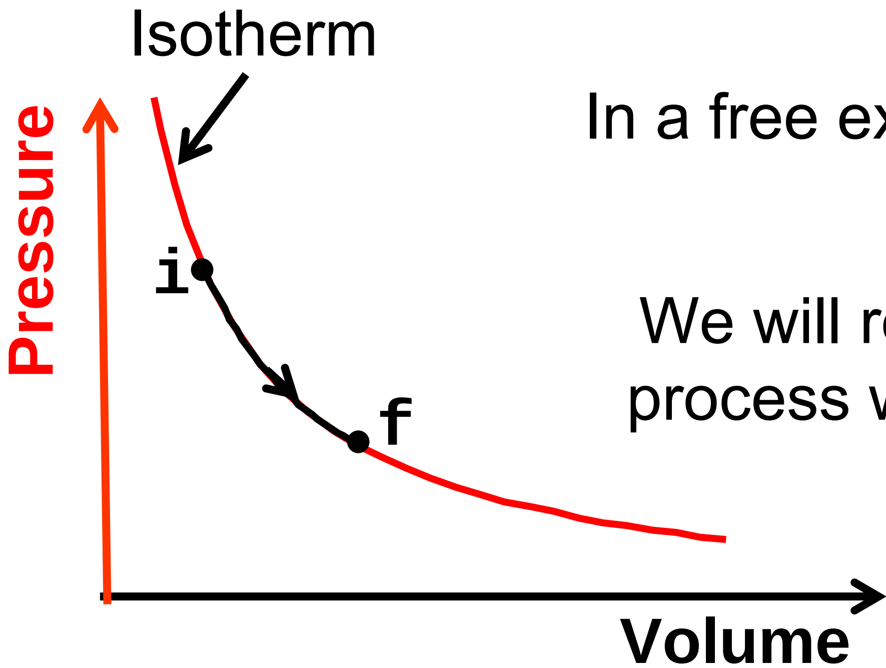


We do not know the volume and pressure at points between the initial and final states

21-2 Change in Entropy

Example: The change in entropy of a free expansion process

Since entropy is a state property,
we will get the same change in entropy,
if we replace the free expansion process (irreversible)
with a reversible process
that connects the initial and final states



In a free expansion process, $T_f = T_i$

We will replace the free expansion process with an isothermal process

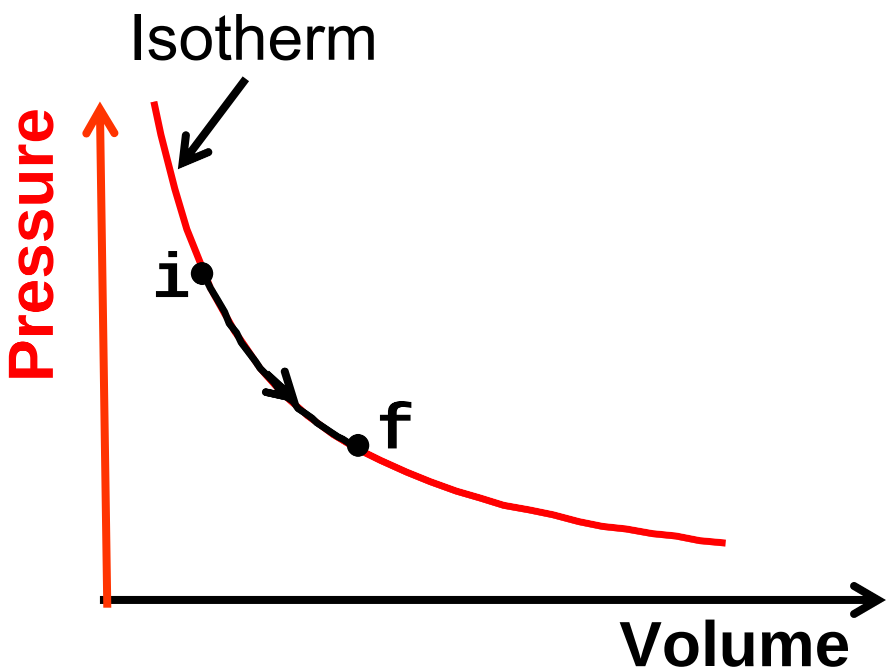
21-2 Change in Entropy

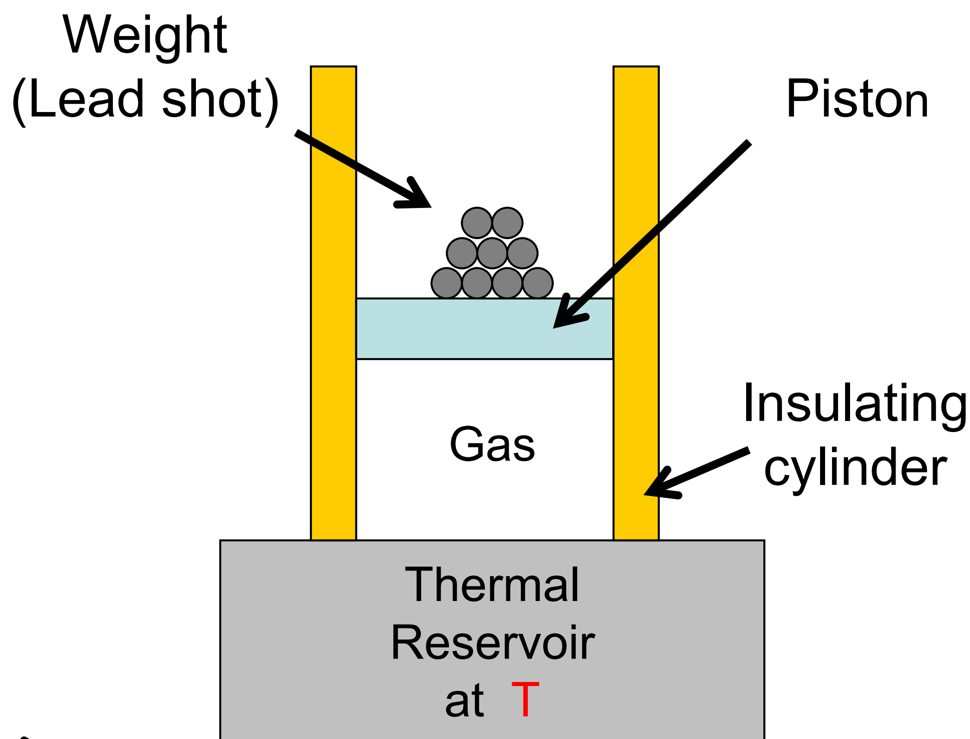
Example: The change in entropy of a free expansion process

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T}$$

For isothermal procss, $Q = W = nRT \ln \frac{V_f}{V_i}$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$





21-2 Change in Entropy

To find the entropy change for an irreversible process occurring in a closed system,
replace that process with any reversible process that connects the same initial and final states.
Calculate the entropy change for this reversible process using

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

21-2 Change in Entropy

For an ideal gas

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

21-2 Change in Entropy

Derivation of $\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$

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

For small changes $dE_{int} = dQ - dW$

$$dQ = dW + dE_{int}$$

$$dQ = pdV + nC_V dT$$

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{pdV}{T} + \int_i^f \frac{nC_V dT}{T}$$

$pV=nRT$

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{nRdV}{V} + \int_i^f \frac{nC_V dT}{T}$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

21-2 Change in Entropy

For a solid or liquid substance for which the temperature changes by ΔT

(no phase transition)

Specific heat

$$\Delta S = m\,c \ln \frac{T_f}{T_i}$$

$$\Delta S = C \ln \frac{T_f}{T_i}$$

Heat capacity

21-2 Change in Entropy

Derivation of $\Delta S = m\, c \ln \frac{T_f}{T_i}$

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

$$\Delta S = m\, c \ln \frac{T_f}{T_i}$$

21-2 Change in Entropy

For a solid or liquid substance that undergoes phase transition at temperature T

Heat of transformation

$$\Delta S = \frac{L\,m}{T}$$

example : liquid to gas

$$\Delta S = \frac{L_F\,m}{T}$$

example : gas to liquid

$$\Delta S = -\frac{L_F\,m}{T}$$

21-2 Change in Entropy

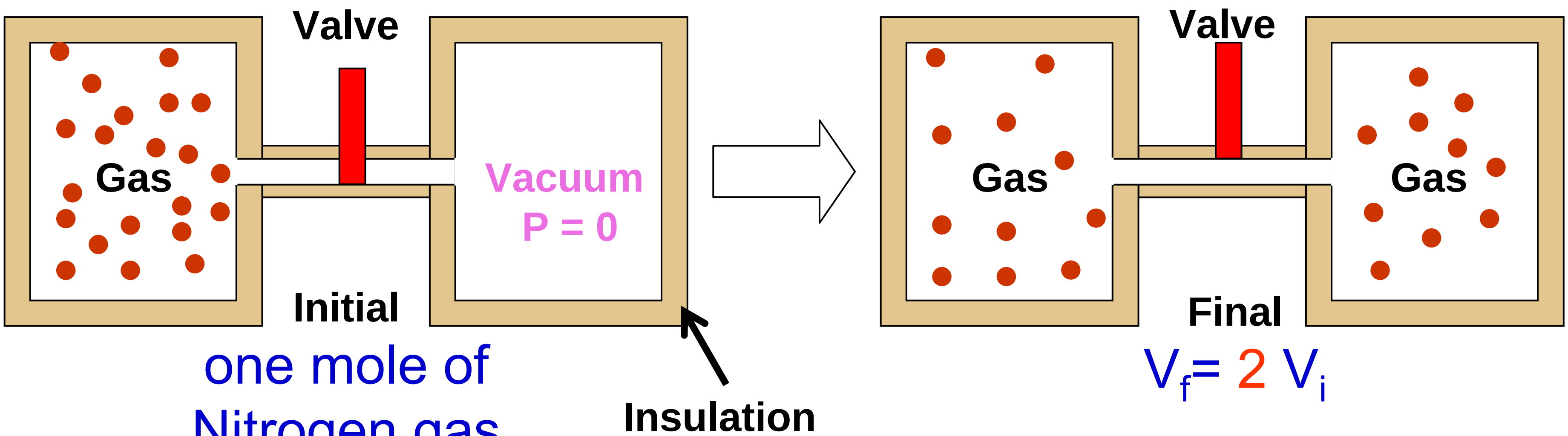
Derivation of $\Delta S = \frac{L\,m}{T}$

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T} = \frac{L\,m}{T}$$

21-2 Change in Entropy

Sample Problem 21-1

Free expansion



one mole of Nitrogen gas

$V_f = 2\,V_i$

The change in entropy?

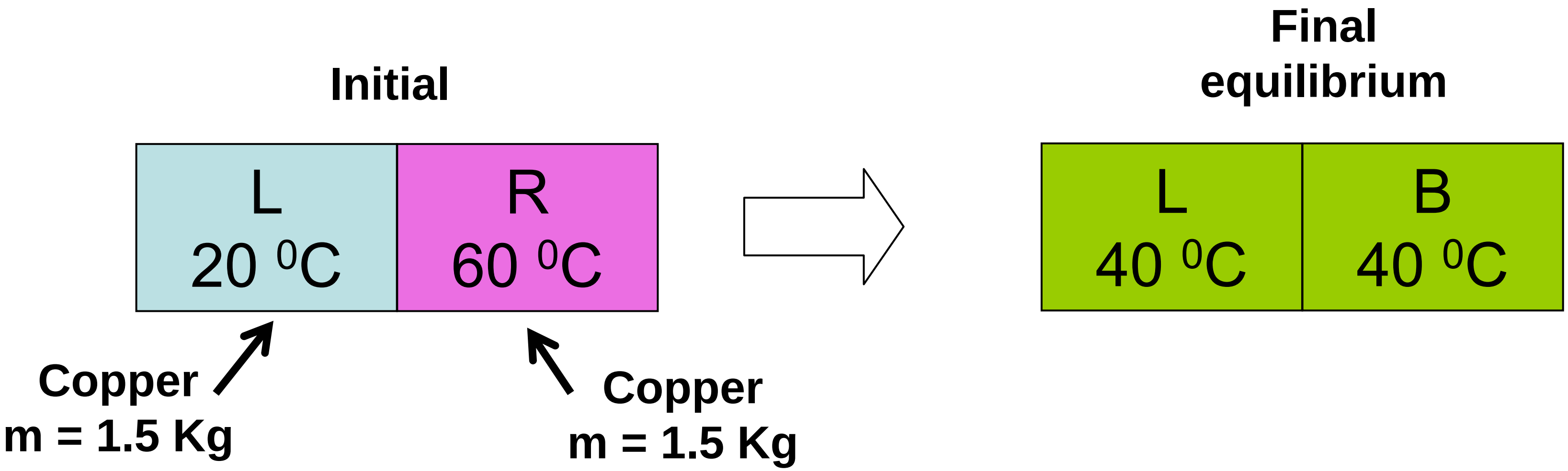
For an ideal gas $\Delta S = nR\ln\dfrac{V_f}{V_i} + nC_v\ln\dfrac{T_f}{T_i}$

For free expansion $T_f = T_i$

$$\Delta S = nR\ln\frac{2V_i}{V_i} = (1\ \text{mol})(8.31\ \text{J/mol}\cdot\text{K})\ln 2 = 5.76\ \text{J/K}$$

21-2 Change in Entropy

Sample Problem 21-2



The change in entropy of the two-block system?

$$\Delta S_L = mc \ln \frac{T_f}{T_{Li}} = (1.5\text{kg})386\text{J/kg} \cdot \text{K}) \ln \frac{40+273}{20+273} = -35.86\text{J/K}$$

$$\Delta S_R = mc \ln \frac{T_f}{T_{Ri}} = (1.5\text{kg})386\text{J/kg} \cdot \text{K}) \ln \frac{40+273}{60+273} = 38.23\text{J/K}$$

$$\Delta S = \Delta S_L + \Delta S_R = 2.4 \text{ J/K}$$

21-2 Change in Entropy

Checkpoint 2

21-3 The Second Law of Thermodynamics

Second Law of Thermodynamics

If a process occurs in a closed system,
the entropy of the system
increases for irreversible processes
and
remains constant for reversible processes.
It never decreases

closed system

$\Delta S > 0$ irreversible processes

$\Delta S = 0$ reversible processes

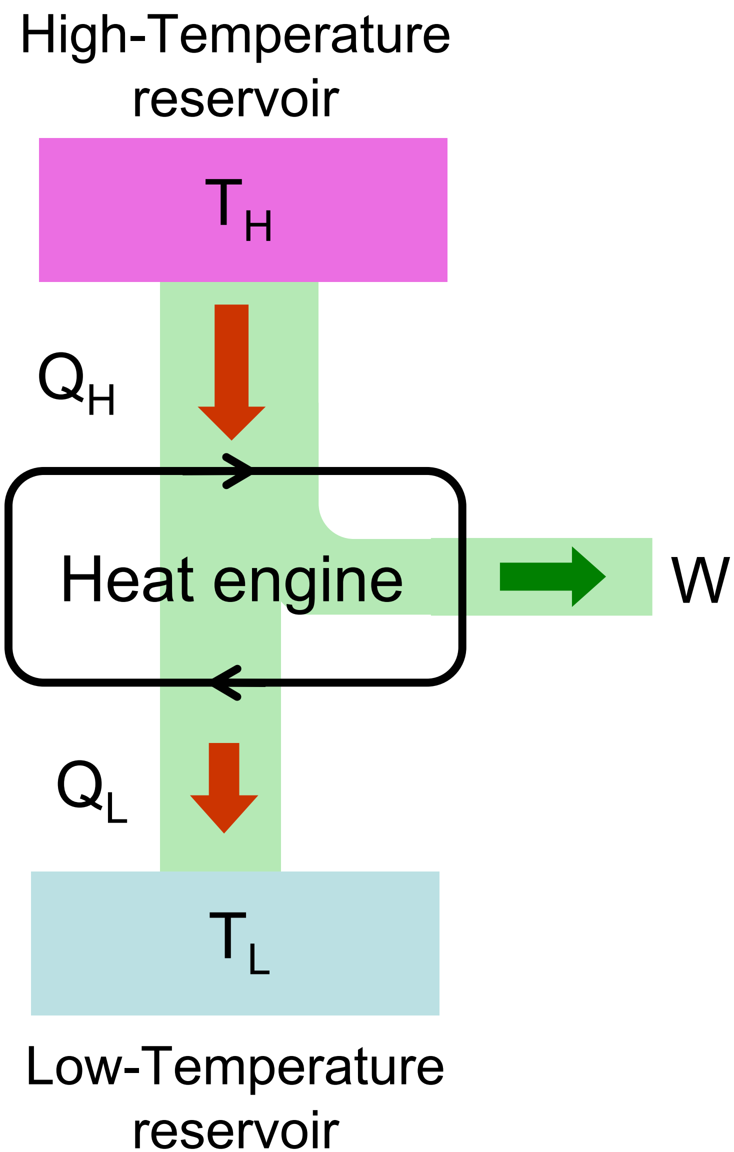
21-4 The Second Law of Thermodynamics

In real world,

almost all processes are irreversible.

Processes in which the system's entropy remains constant are always idealization.

21-4 Entropy in the Real World: Engines



	Working substance
Steam engine	Water-gas
Car engine	Gasoline-air

21-4 Entropy in the Real World: Engines

Ideal engine

In an ideal engine all processes are reversible and no wasteful energy transfer occur due, say, friction and turbulence

Pronounced "Car-no"

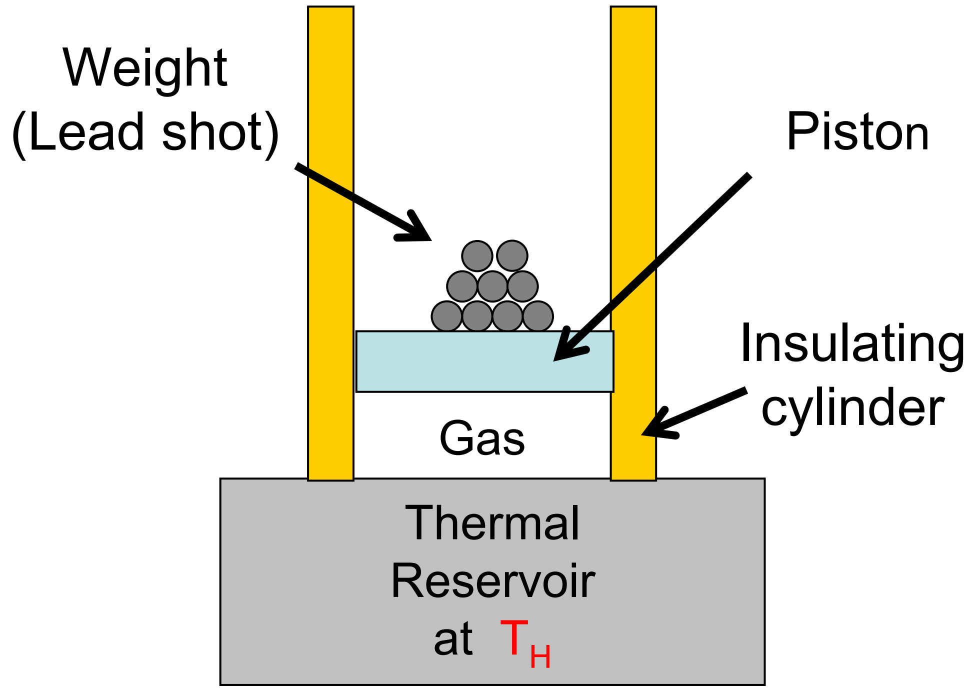
Carnot Engine.

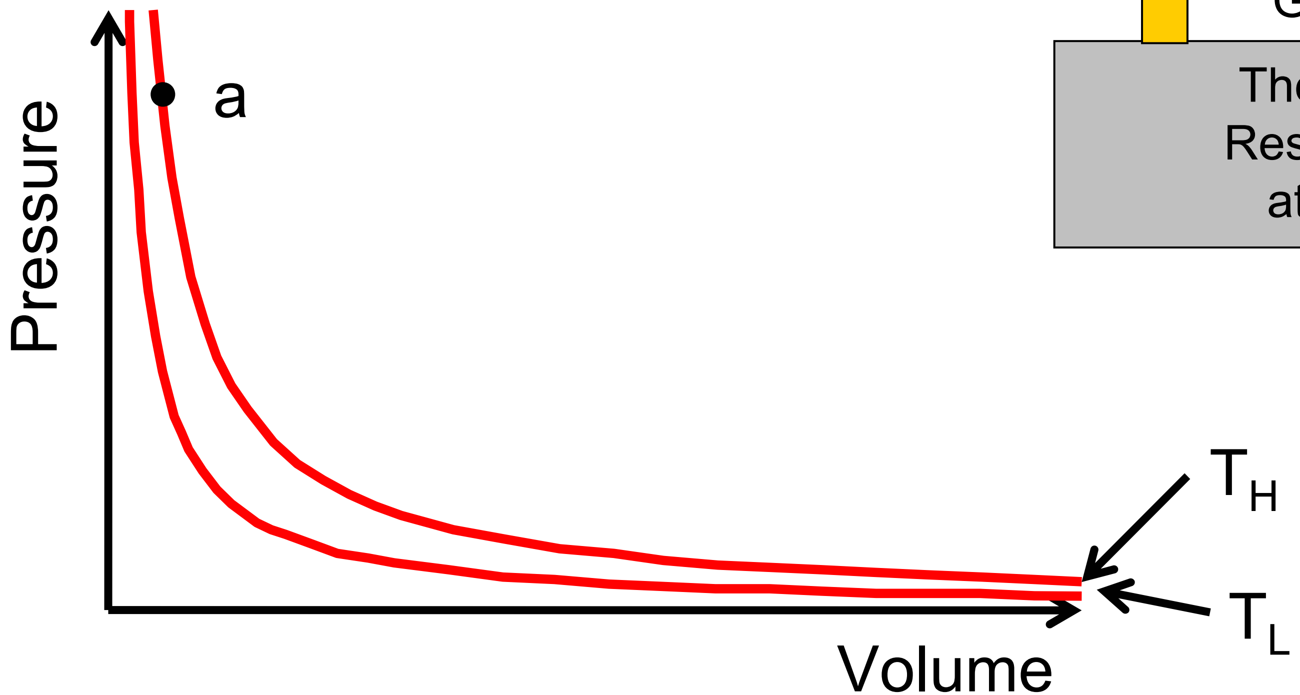
Carnot engine is an ideal engine.
Carnot engine is the best engine in using energy as heat to do useful work.
You can not build more efficient heat engine than a Carnot engine.

21-4 Entropy in the Real World: Engines

Carnot Engine

Start at state a

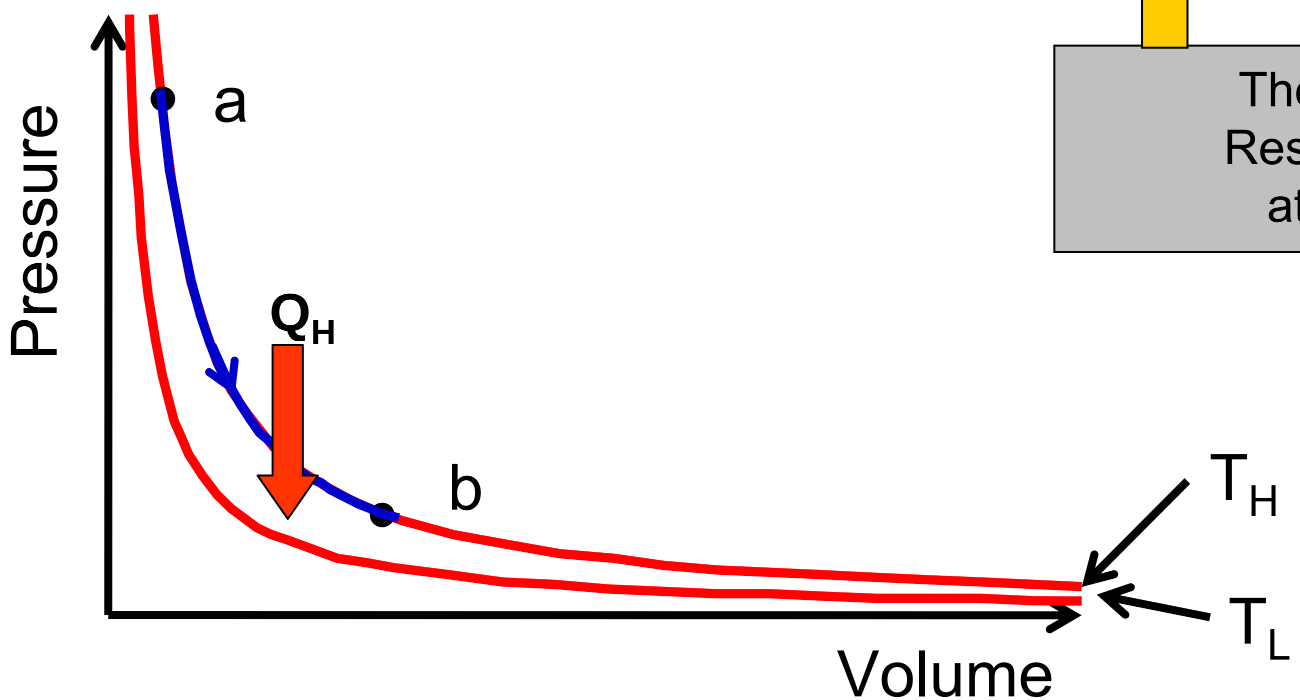


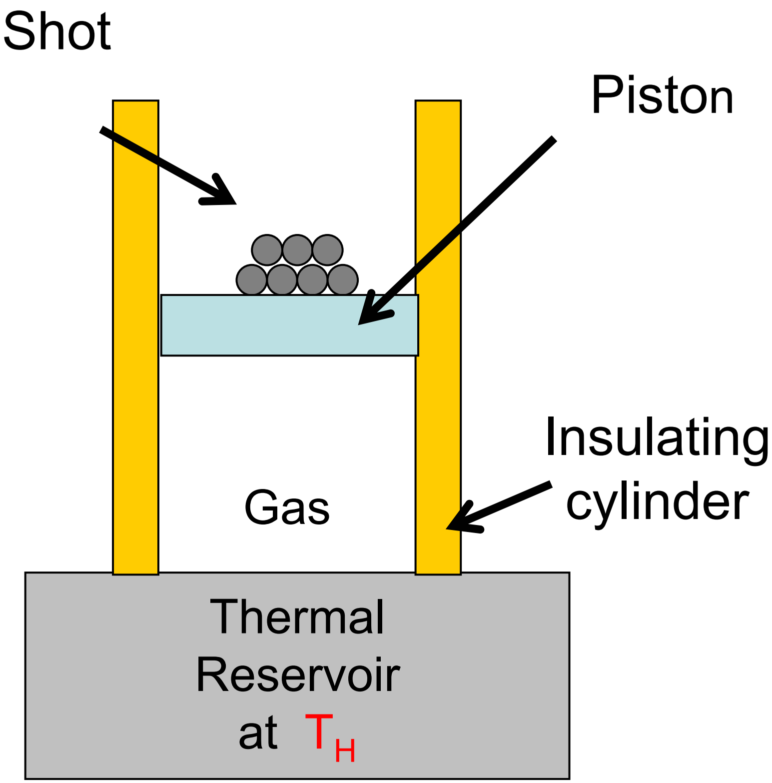


21-4 Entropy in the Real World: Engines

Carnot Engine

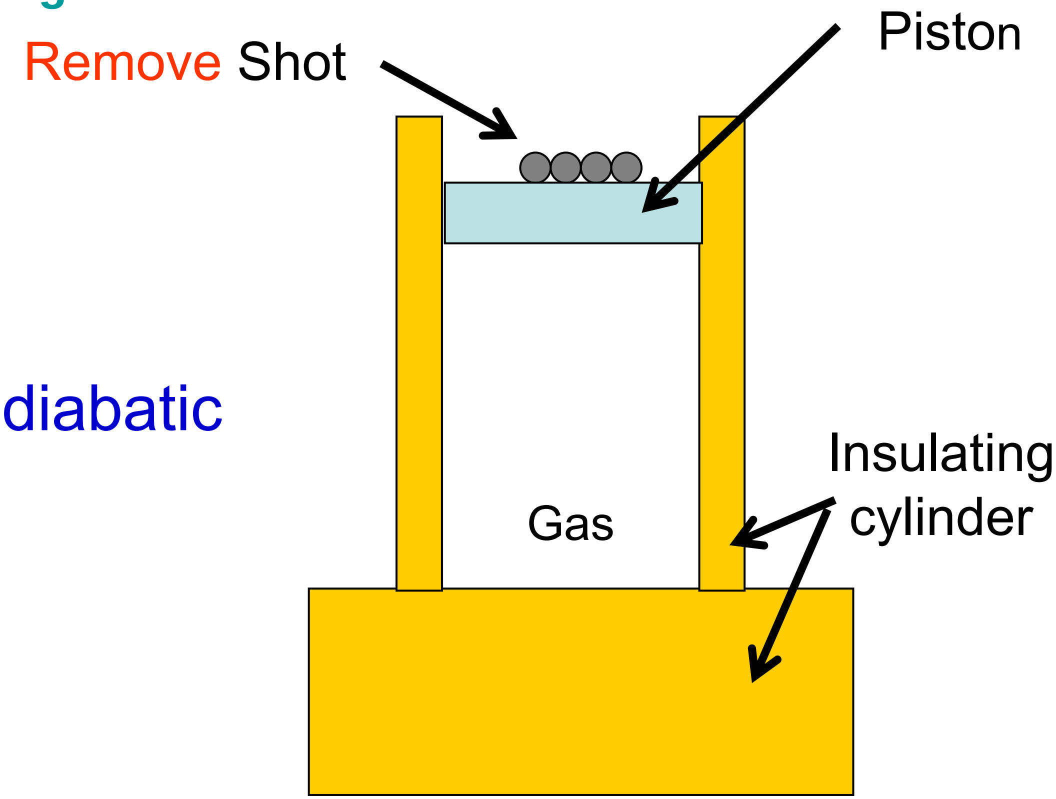
Stroke a → b isothermal



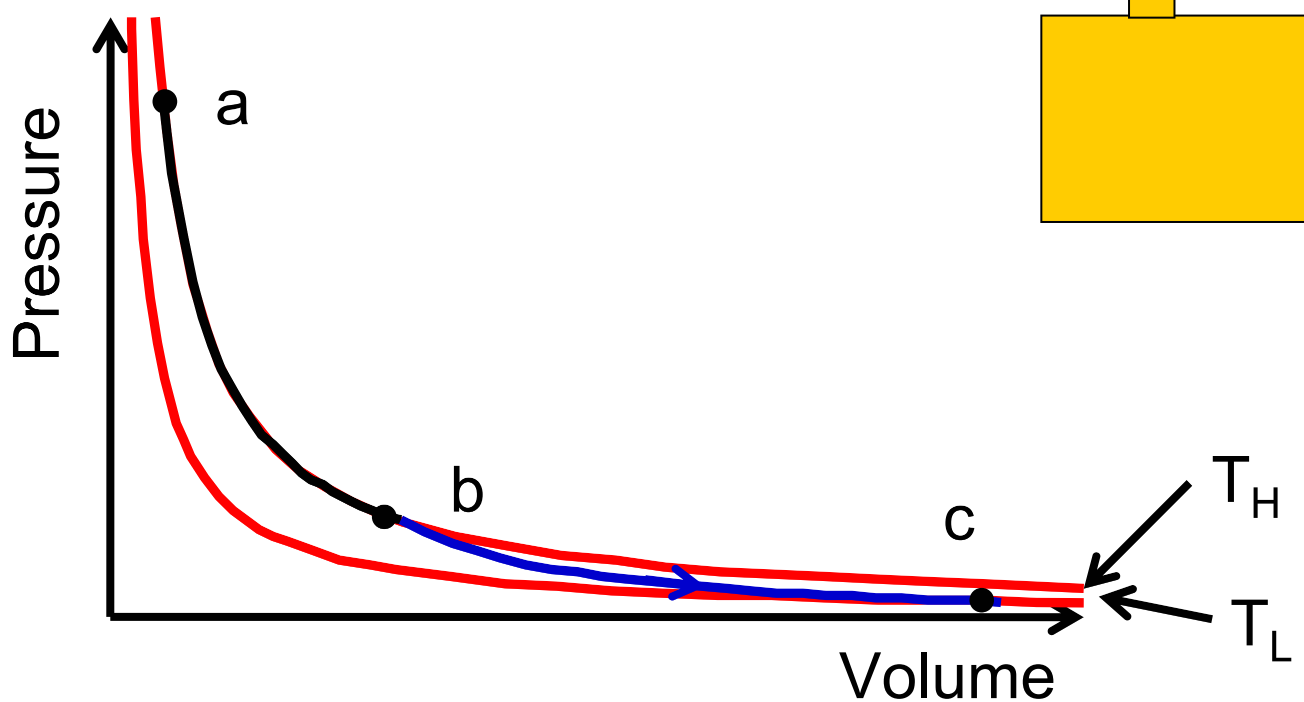


21-4 Entropy in the Real World: Engines

Carnot Engine



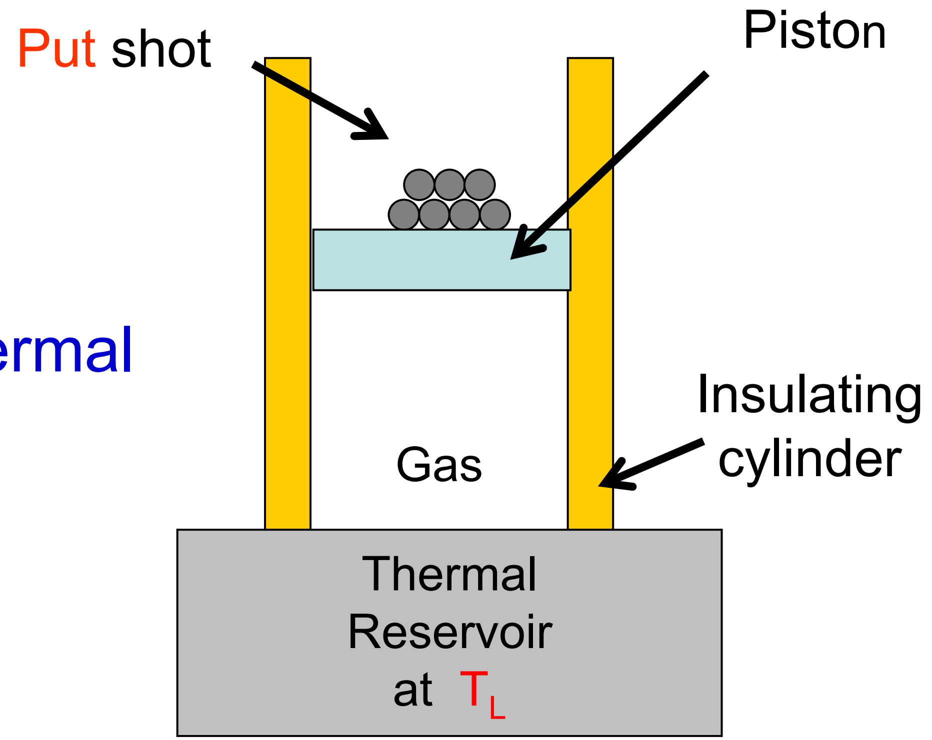
Stroke b → c adiabatic

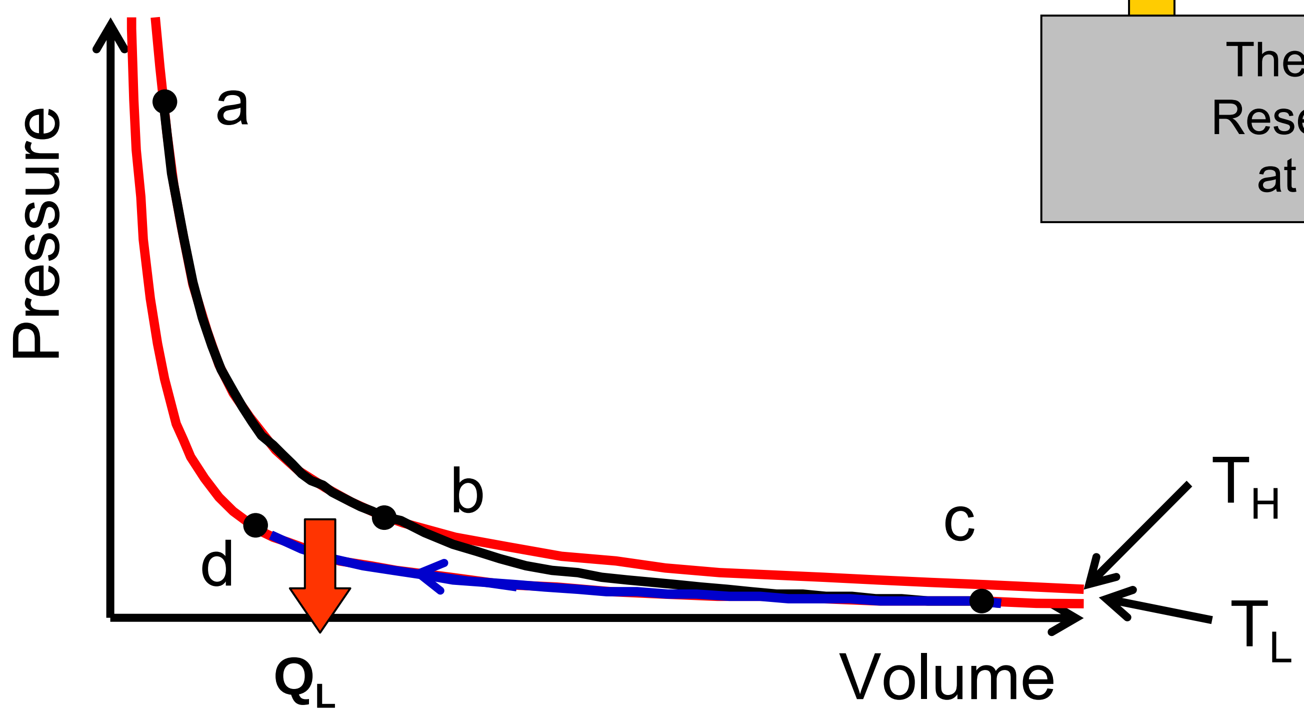


21-4 Entropy in the Real World: Engines

Carnot Engine

Stroke c → d isothermal

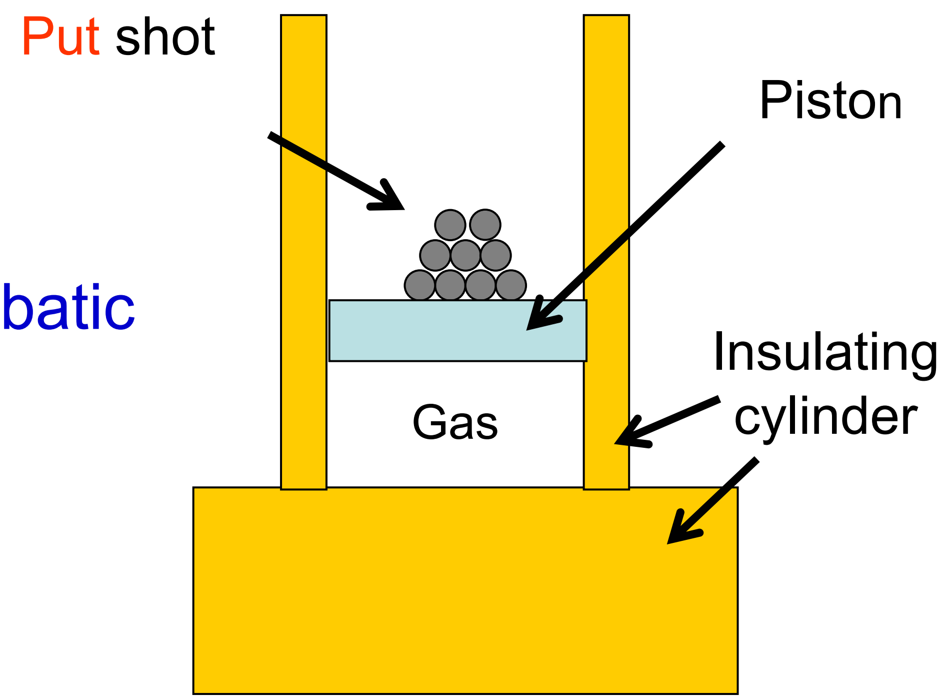


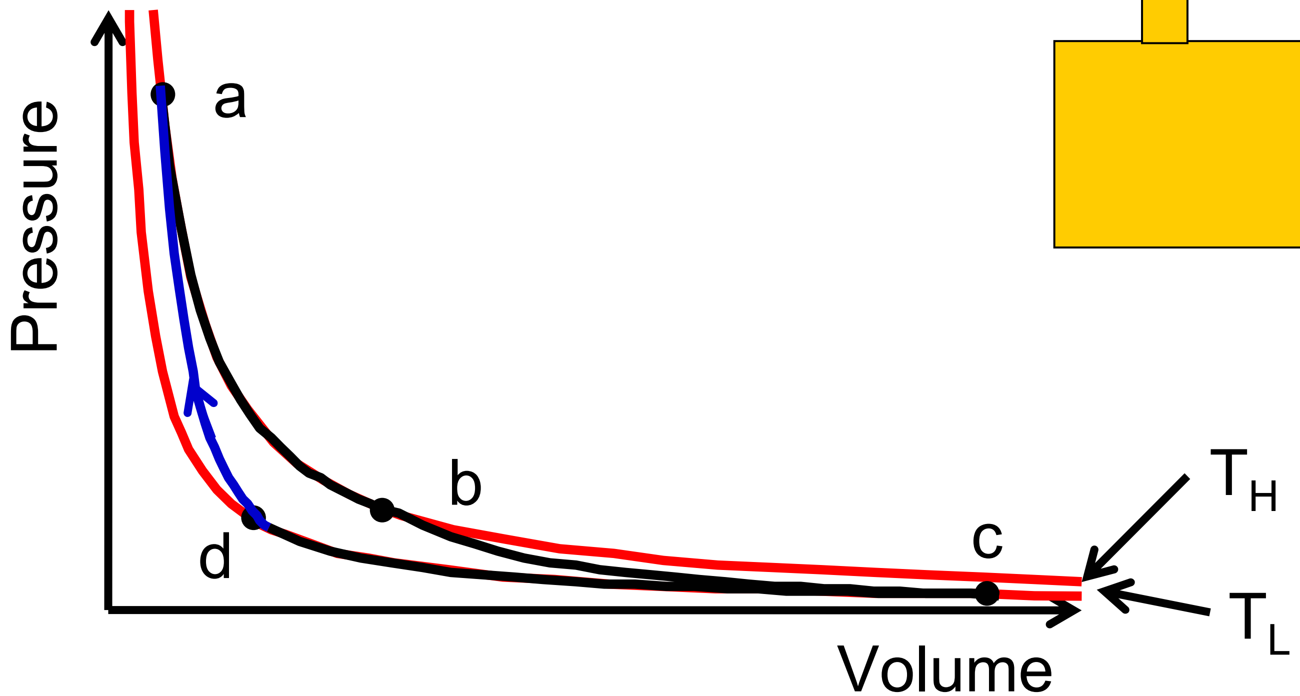


21-4 Entropy in the Real World: Engines

Carnot Engine

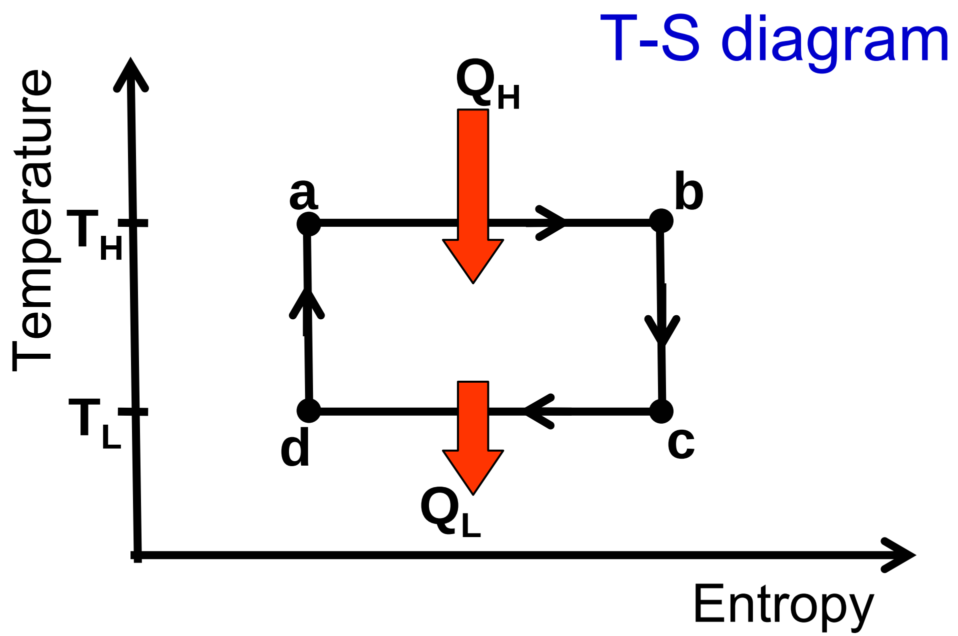
Stroke d → a adiabatic

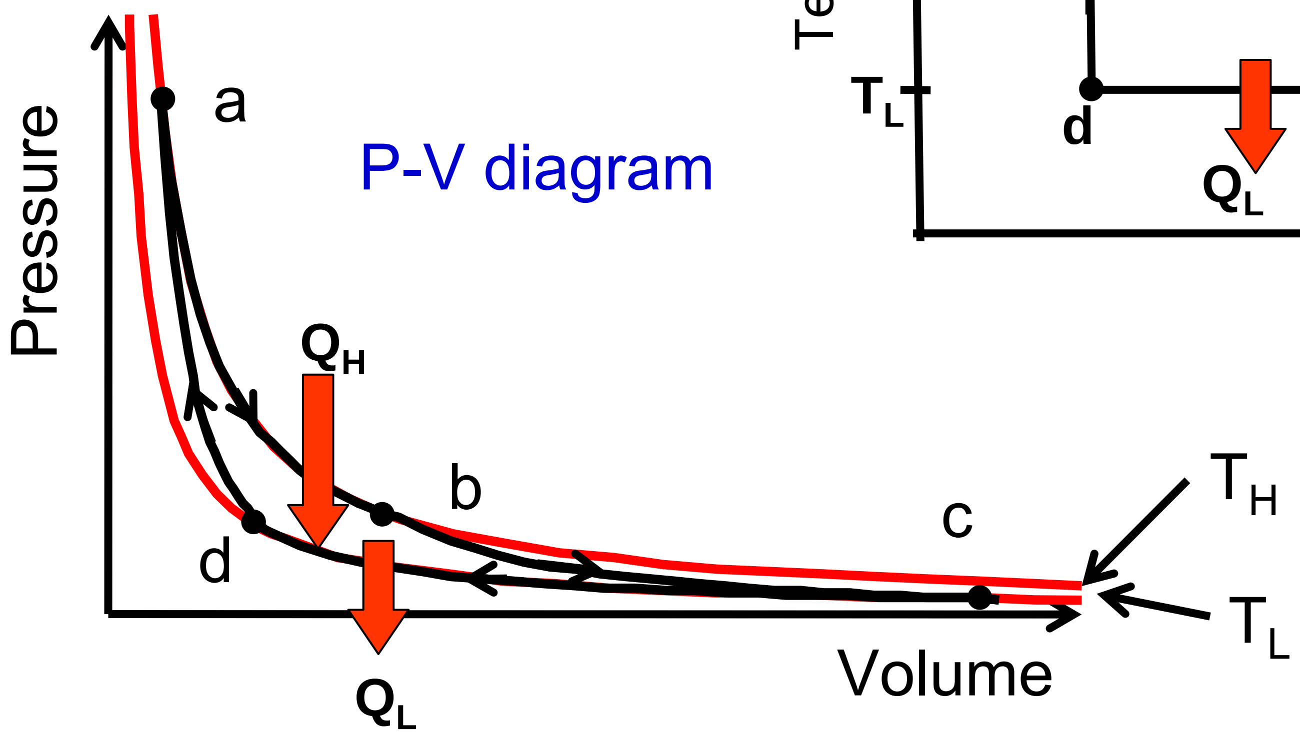




21-4 Entropy in the Real World: Engines

Entropy change for a Cronot engine





21-4 Entropy in the Real World: Engines

Work done by a Cronot engine during a cycle

First law of Thermodynamics $\Delta E_{int} = Q - W$

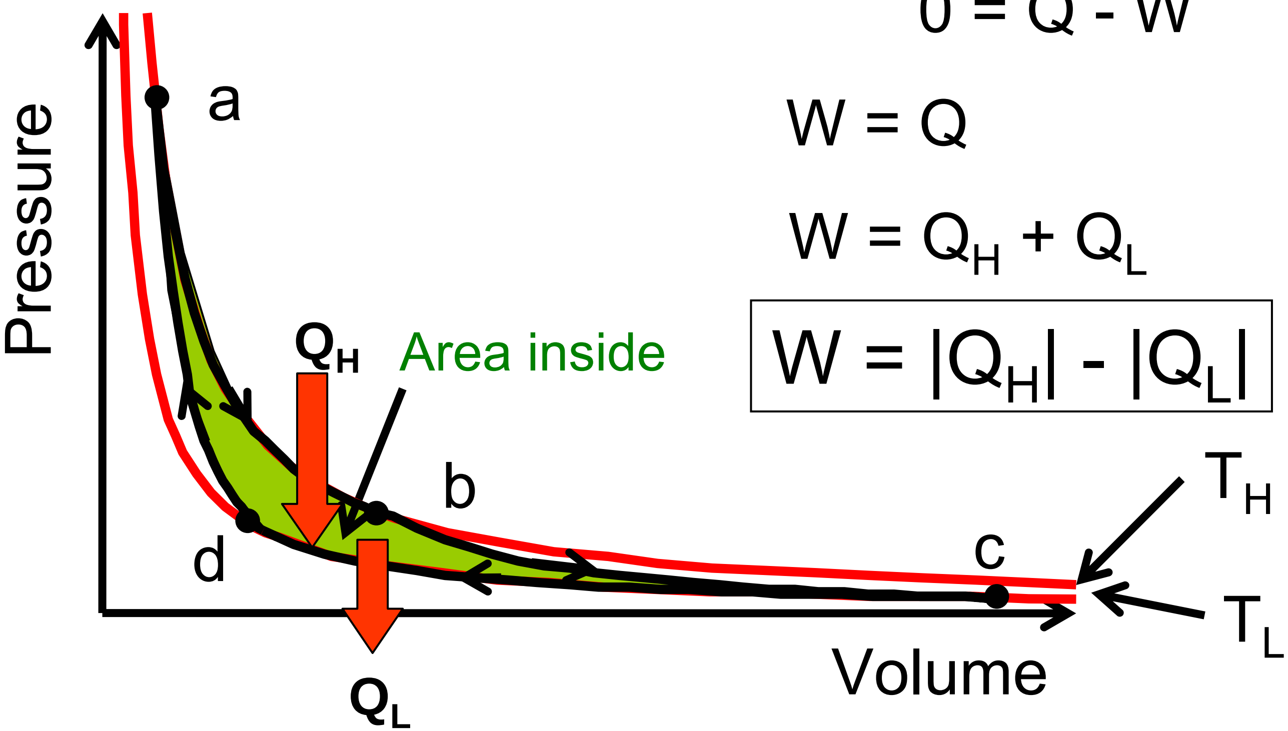
For a cyclic process $\Delta E_{int} = 0$

$$0 = Q - W$$

$$W = Q$$

$$W = Q_H + Q_L$$

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



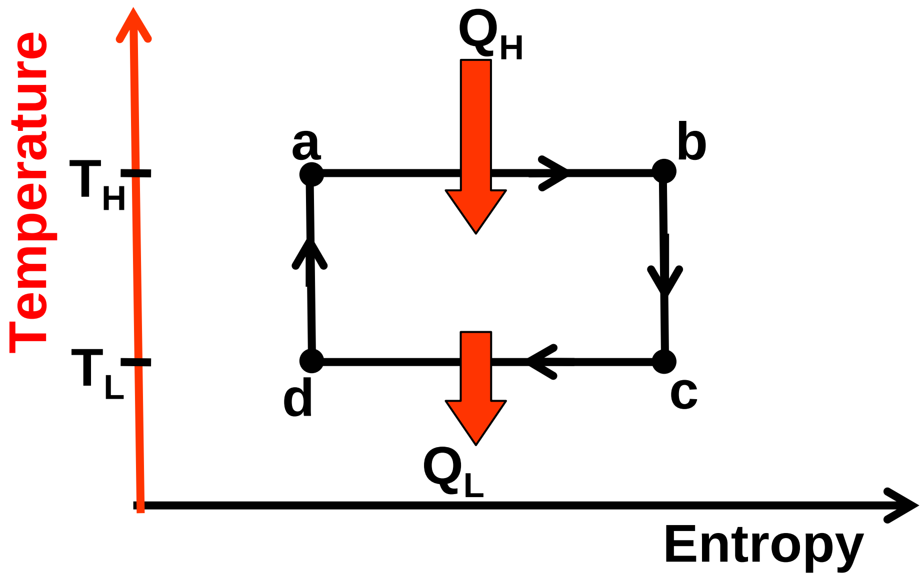
21-4 Entropy in the Real World: Engines

Entropy change of a Cronot engine per cycle

$$\Delta S = \Delta S_H + \Delta S_L$$

$$\Delta S = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

Heat is removed



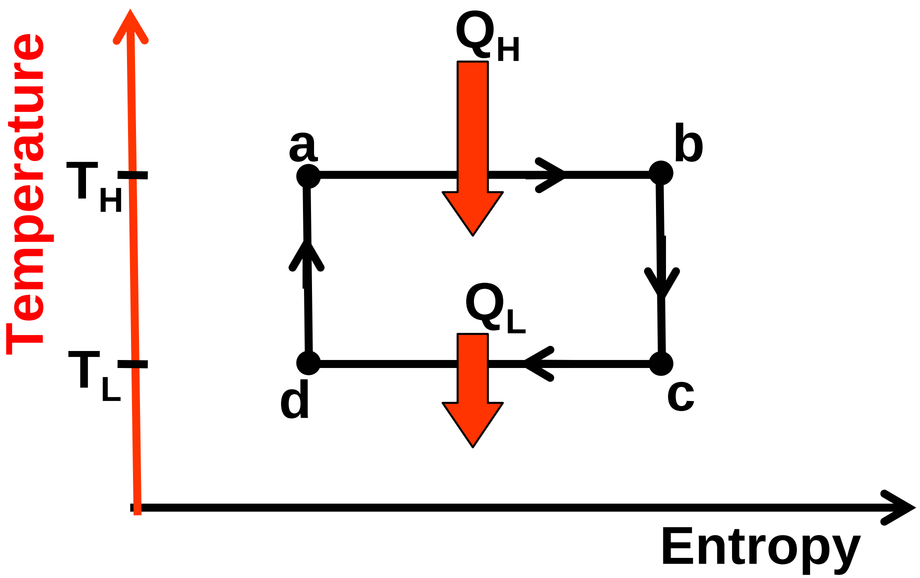
For a cyclic process $\Delta S = 0$

$$0 = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

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

21-4 Entropy in the Real World: Engines

Entropy change of a Cronot engine per cycle



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

Since $T_H > T_L$, more energy is extracted from the high temperature reservoir than delivered to the low-temperature reservoir

$$T_H > T_L \quad \rightarrow \quad |Q_H| > |Q_L|$$

21-4 Entropy in the Real World: Engines

Thermal efficiency of an engine

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|}$$

any engine

Thermal efficiency of a Carnot engine

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

$$\boxed{\varepsilon_C = 1 - \frac{T_L}{T_H}}$$

Carnot engine

21-4 Entropy in the Real World: Engines

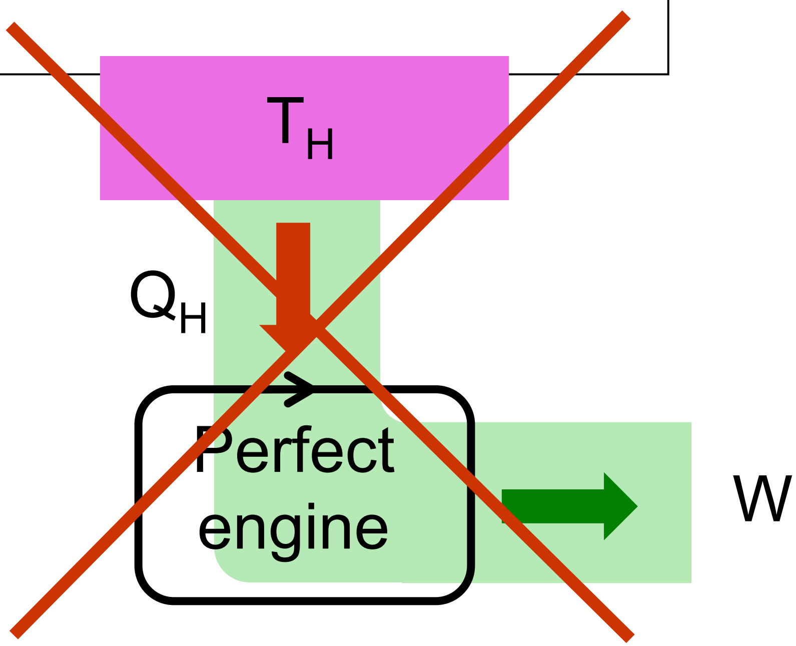
Thermal efficiency of a Carnot engine

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

$\varepsilon_C = 1$ when $T_L = 0$ K or $T_H = \infty$, which are impossible conditions

No series of processes are possible whose sole result is the transfer of energy as heat from thermal reservoir and the complete conversion of this energy to work

There are no perfect engines



21-4 Entropy in the Real World: Engines

Thermal efficiency of a Carnot engine

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

Always less than unity
(less than 100%)

No real engine can have efficiency greater than ε_C

Real engines have efficiencies less than ε_C because the processes that form their cycles are irreversible

If your car were powered by a Carnot engine, it would have an efficiency of bout 55%; its actual efficiency is probably about 25%.

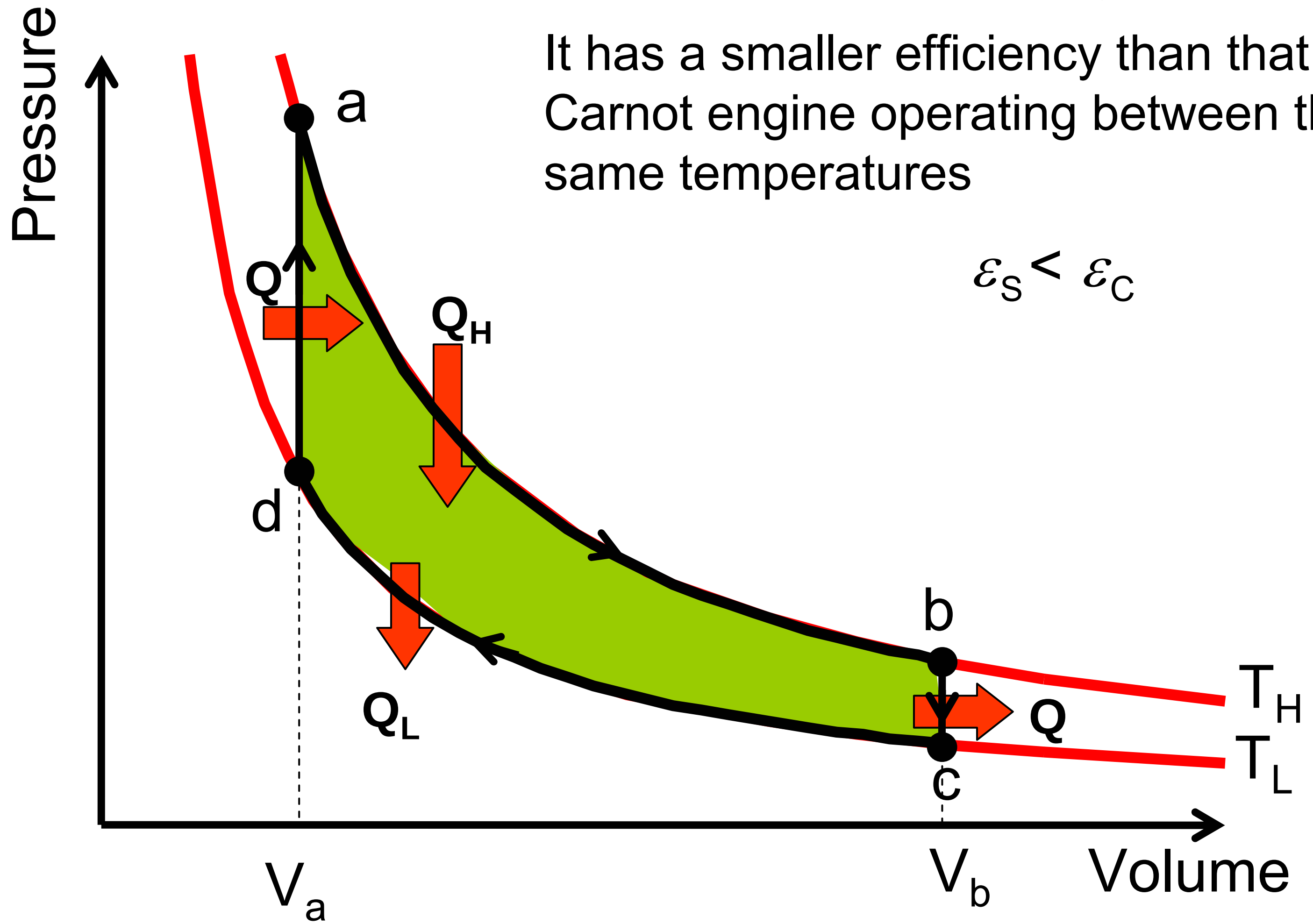
21-4 Entropy in the Real World: Engines

Stirling engine

It is an ideal engine

It has a smaller efficiency than that of a Carnot engine operating between the same temperatures

$$\varepsilon_S < \varepsilon_C$$



21-4 Entropy in the Real World: Engines

Checkpoint 3

$$\varepsilon_C = 1 - \frac{400}{500} = 0.2$$

$$\varepsilon_C = 1 - \frac{600}{800} = 0.25$$

$$\varepsilon_C = 1 - \frac{400}{600} = 0.33$$

21-4 Entropy in the Real World: Engines

Sample Problem 21-3

Carnot engine

$T_H = 850$ K

$T_L = 300$ K

W = 1200 J per cycle

Each cycle takes 0.25 s

What is the efficiency of this engine?

$$\varepsilon_C = 1 - \frac{300}{850} = 0.65 = 65\%$$

What is the average power of this engine?

$$P = \frac{W}{t} = \frac{1200\ \text{J}}{0.25\ \text{s}} = 4.8\text{KW}$$

21-4 Entropy in the Real World: Engines

Sample Problem 21-3

How much energy $|Q_H|$ is extracted as heat form the high-temperature reservoir every cycle?

$$\varepsilon = \frac{W}{|Q_H|} \rightarrow |Q_H| = \frac{W}{\varepsilon} = \frac{1200\text{ J}}{0.647} = 1855\text{ J}$$

How much energy $|Q_L|$ is delivered as heat to the low-temperature reservoir every cycle?

$$W = |Q_H| - |Q_L| \rightarrow$$

$$|QL| = |Q_H| - W = 1855\text{ J} – 1200\text{ J} = 655\text{ J}$$

21-4 Entropy in the Real World: Engines

Sample Problem 21-3

What is the entropy change of the working substance for the energy transfer to it from the high-temperature reservoir ?

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855\ \text{J}}{850\ \text{K}} = 2.18\ \text{J/K}$$

What is the entropy change of the working substance for the energy transfer to it from the low-temperature reservoir ?

$$\Delta S_H = \frac{Q_L}{T_L} = \frac{-655\ \text{J}}{300\ \text{K}} = -2.18\ \text{J/K}$$

21-4 Entropy in the Real World: Engines

Sample Problem 21-4

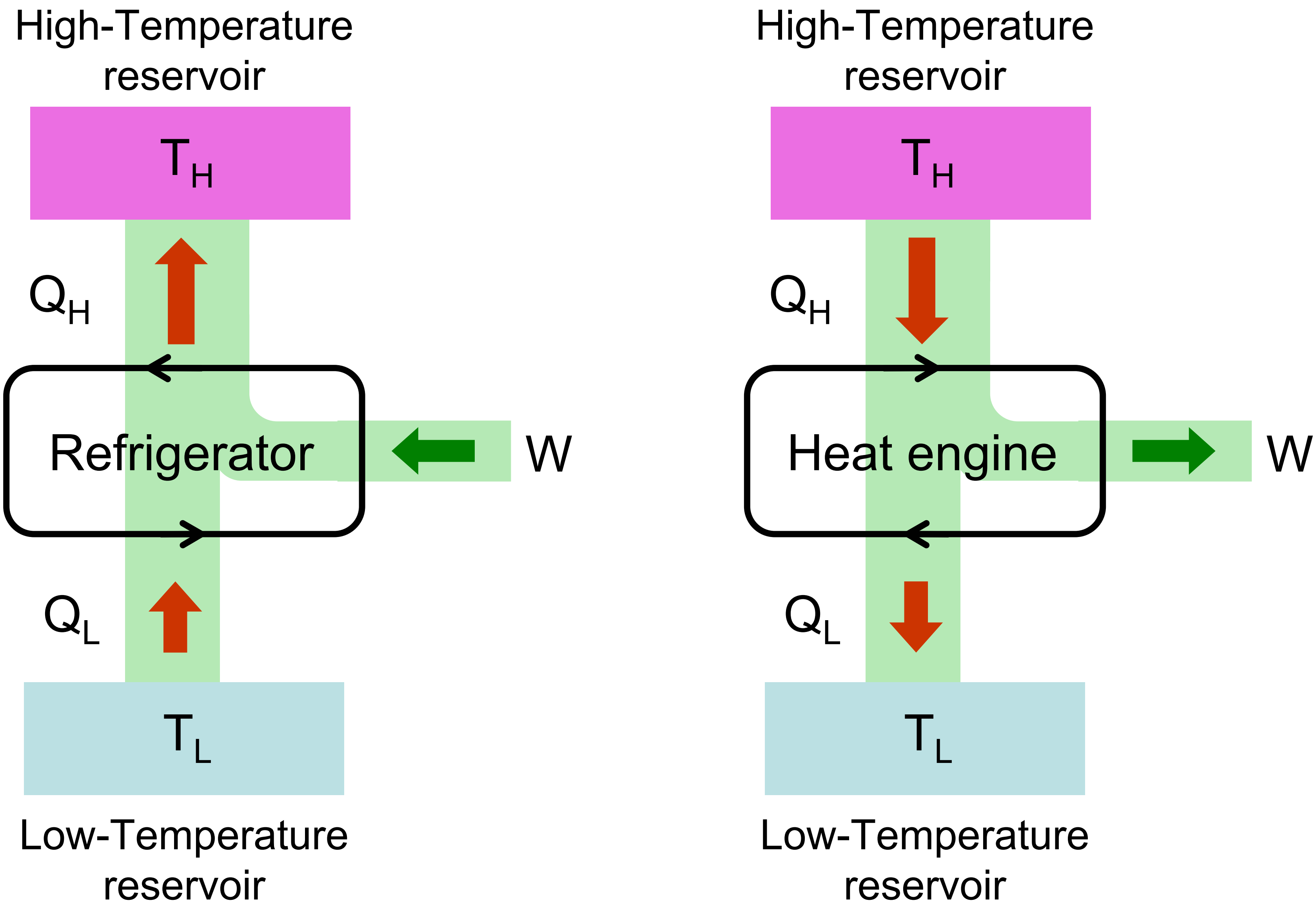
Is it possible for an engine operated between the boiling and freezing points of water to have an efficiency of 75%?

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{(0+237)\text{K}}{(100+273)\ \text{K}} = 0.27 = 27\%$$

It can not be

21-4 Entropy in the Real World: Refrigerator

Refrigerator



21-4 Entropy in the Real World: Refrigerator

Ideal refrigerator

In an ideal refrigerator, all processes are reversible and no wasteful energy transfer occur due, say, friction and turbulence

Coefficient of performance

We want to extract as much energy $|Q_L|$ as possible from the low-temperature reservoir (what we want) for the least amount of work $|W|$ (what we pay)

Coefficient of performance

$$K = \frac{\text{What we want}}{\text{What we pay}} = \frac{|Q_L|}{|W|}$$

21-4 Entropy in the Real World: Refrigerator

Coefficient of performance

$$K = \frac{\text{What we want}}{\text{What we pay}} = \frac{|Q_L|}{|W|}$$

For typical room air conditioner $K \approx 2.5$
For typical household refrigerator $K \approx 5$

A Carnot refrigerator operates in the reverse of the Carnot engine

$$W = |Q_H| - |Q_L| \qquad \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

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

$$\boxed{K_C = \frac{T_L}{T_H - T_L}}$$

Coefficient of performance of a Carnot refrigerator

21-4 Entropy in the Real World: Refrigerator

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

Coefficient of performance of a Carnot refrigerator

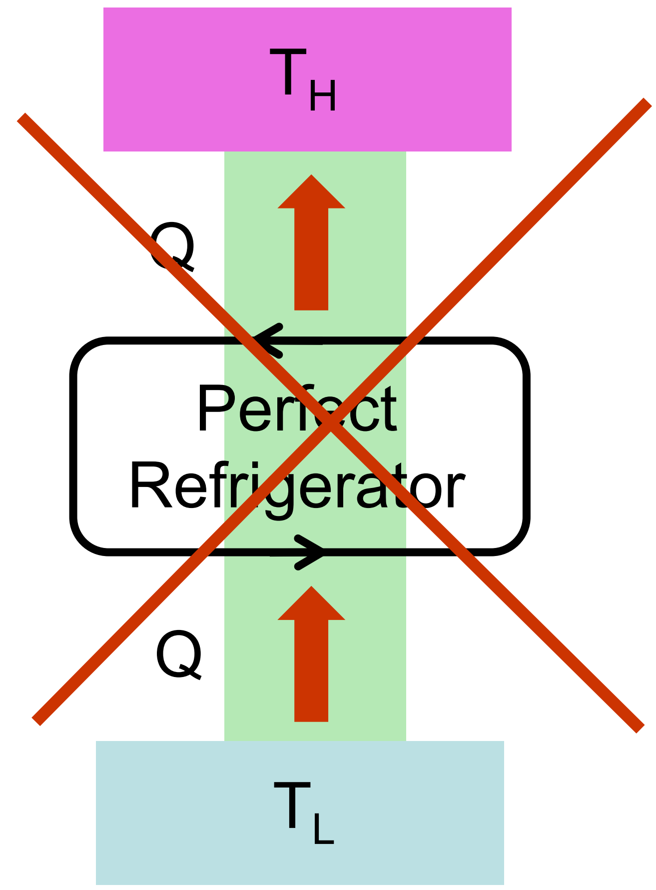
The value of K_C is higher the closer the temperatures of the two reservoirs to each other.

For $T_H > T_L$, $K_C > 1$.

21-4 Entropy in the Real World: Refrigerator

Why perfect refrigerators are impossible?

A perfect refrigerator transfer heat Q form a cold reservoir to a warm reservoir without the need for work



21-4 Entropy in the Real World: Refrigerator

Why perfect refrigerators are impossible?

Let us assume it is possible to have a perfect refrigerator

$$\Delta S = \frac{|Q|}{T_H} - \frac{|Q|}{T_L}$$

Since $T_H > T_L$ → $\Delta S < 0$

This violates the second law of thermodynamics. The change in entropy for the closed system (refrigerator + reservoirs) can not be negative

→ Perfect refrigerators do not exist

→ Perfect refrigerators violate the second law of thermodynamics

21-4 Entropy in the Real World: Refrigerator

the second law of thermodynamics

closed system

$\Delta S > 0$ irreversible processes

$\Delta S = 0$ reversible processes

Another formulation of the second law of thermodynamics

No series of processes are possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature

21-4 Entropy in the Real World: Refrigerator

Checkpoint 4

Let the temperature change = dT

a- $K_C = \dfrac{T_L + dT}{T_H - (T_L + dT)}$ 1

b- $K_C = \dfrac{T_L - dT}{T_H - (T_L - dT)}$ 4

c- $K_C = \dfrac{T_L}{T_H + dT - T_L}$ 3

d- $K_C = \dfrac{T_L}{T_H - dT - T_L}$ 2