Second law of thermodynamics

- <u>Kelvin & Planck Statement</u>

  No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work.

- <u>Clausius Statement</u>

  No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.

Entropy and the 2nd law

The entropy of an isolated system may increase but can never decrease.

$$\Delta S \geq 0$$

- The total entropy of an isolated system is constant when the process is reversible.
- When an irreversible process occurs, the total entropy of an isolated system increases.

Is it a violation of the second law of thermodynamics to convert mechanical energy completely into heat?

A. Yes
B. No

Is it a violation of the second law of thermodynamics to convert heat completely into work?

A. Yes
B. No

Heat engines

A heat engine takes heat Q from a source, converts part of it to work W, and discards the remainder at a lower temperature.

By definition, an engine undergoes a sequence of processes that eventually leaves the system in the same state in which it started.

For any cyclic process, the first law of thermodynamics requires that the net heat flowing into the engine in a cyclic process equals the net work done by the engine.

$$Q = W \quad \text{where} \quad \Delta U_{\text{int}} = 0$$

Thermal efficiency of heat engines

The **thermal efficiency** of an engine is the quotient

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

We may substitute our relationship for the work of an engine

$$W = Q = Q_H + Q_C = |Q_H| - |Q_C|$$

to get

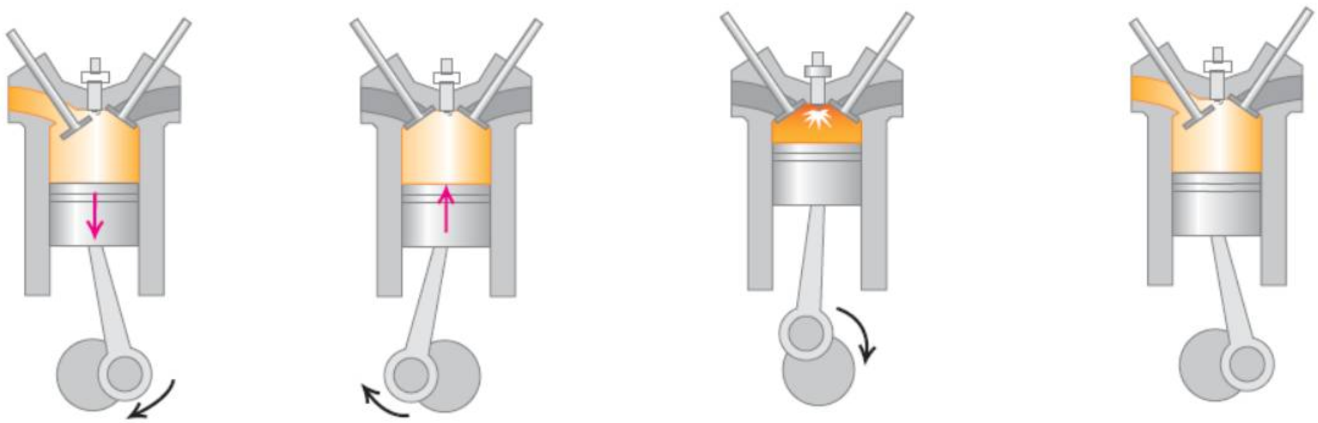
$$e = 1 - \frac{|Q_C|}{|Q_H|}$$

$Q_H =$ heat absorbed by the engine

$Q_C =$ heat rejected by the engine

Otto cycle

The idealized model of the thermodynamic processes in a gasoline engine is the Otto cycle.



<u>Otto cycle steps</u>:

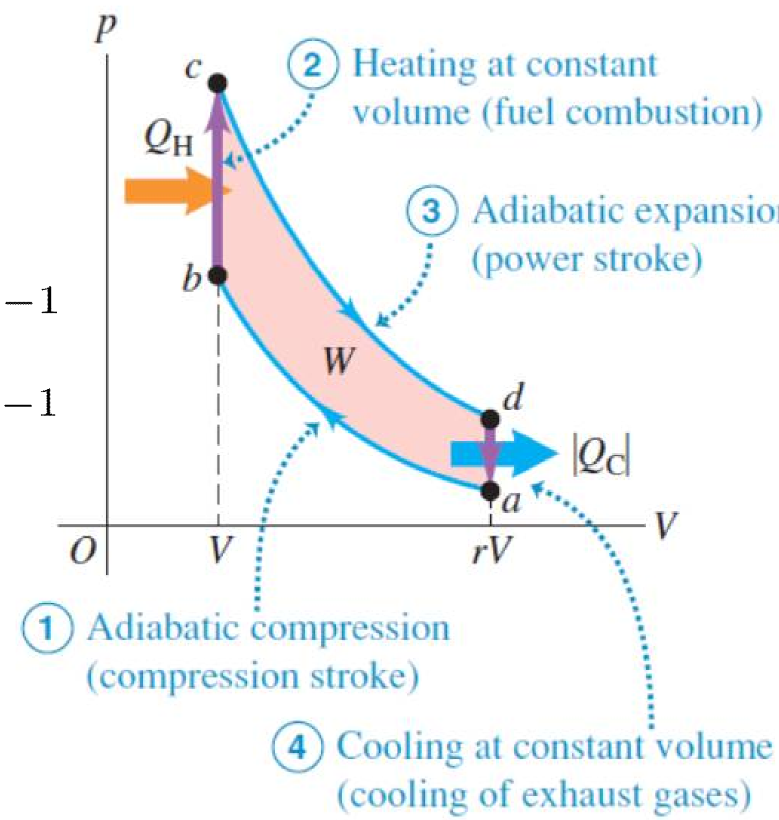
1. The gasoline–air mixture enters the cylinder
2. The mixture is compressed adiabatically and then ignited
3. Heat Q_H is added to the system by the burning gasoline
4. the power stroke is the adiabatic expansion to move the piston back to its original position

Efficiency of the Otto engine

For processes at constant volume the heats have the relationship

$$\begin{cases} Q_H = nC_v\,(T_c - T_b) \\ Q_C = nC_v\,(T_a - T_d) \end{cases}$$

Taking the ratio gives $\dfrac{Q_C}{Q_H} = \dfrac{T_a - T_d}{T_c - T_b}$



The two adiabatic processes give

$$\begin{cases} T_a(rV)^{\gamma-1} = T_b V^{\gamma-1} \\ T_d(rV)^{\gamma-1} = T_c V^{\gamma-1} \end{cases}$$

Therefore, $e = 1 - \dfrac{1}{r^{\gamma-1}}$

Entropy in irreversible processes

In a closed system, the total entropy change during an irreversible cycle is greater than zero.

$$\Delta S = \int \frac{dQ}{T} > 0$$

The entropy change of the system undergoing a reversible process is path independent; however, the entropy change of a system undergoing an irreversible process depends on the path.

Entropy is **NOT** a conserved quantity!!!

Example

Suppose 1.00 kg of water at 90 ^{o}C is placed in thermal contact with 1.00 kg of water at 10 ^{o}C. The end result is 2.00 kg of water at 50 ^{o}C. [C_w = 4190 J/kg]

(a) What is the change of entropy of the hot water, ΔS_H?

(b) What is the change of entropy of the cold water, ΔS_C?

(c) What is the total change of entropy?

Carnot cycle

The Carnot cycle is an idealized heat engine that has the maximum possible efficiency consistent with the second law.

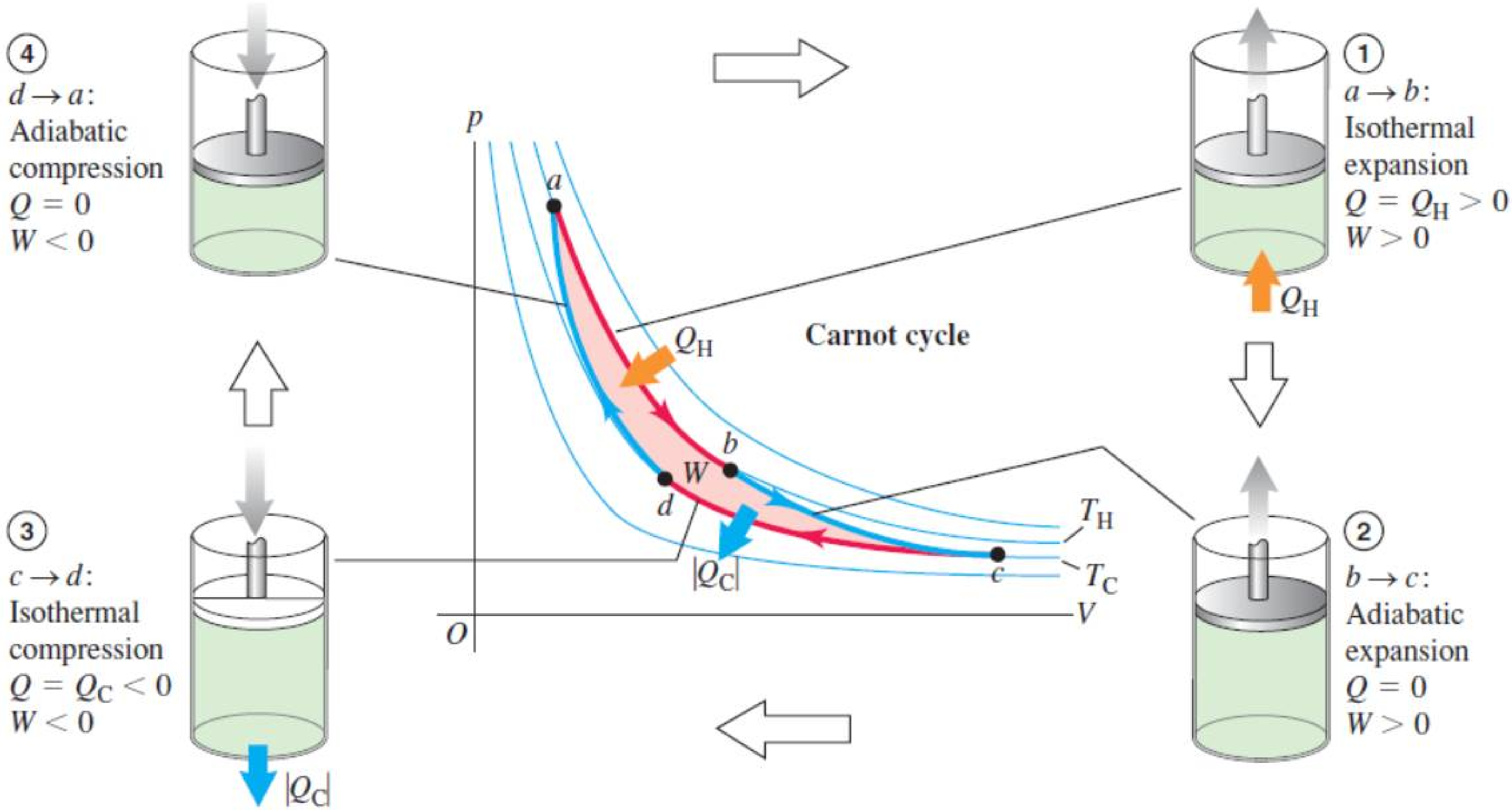
The Carnot cycle takes advantage of the idea of a reversible process, *i.e.*, no heat flow to a reservoir until the engine reaches the reservoir's temperature.

(heat exchanges must occur at same temperature; <u>isothermal</u> and <u>adiabatic</u>)

<u>Carnot cycle steps</u>:

1. The gas expands isothermally at temperature T_H absorbing heat Q_H
2. It expands adiabatically until its temperature drops to T_C
3. It is compressed isothermally at T_C rejecting heat Q_C
4. It is compressed adiabatically back to its initial state at temperature T_H

Carnot cycle PV diagram



Efficiency of the Carnot engine

For isothermal expansion, $\Delta U = 0$, and

$$\begin{cases} Q_H = W_{ab} = nRT_H \ln \dfrac{V_b}{V_a} \\ Q_C = W_{cd} = nRT_C \ln \dfrac{V_d}{V_c} \end{cases}$$

Taking the ratio gives $\dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H}\dfrac{\ln V_c/V_d}{\ln V_b/V_a}$

The temperature–volume relationship for an adiabatic processes gives

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Therefore, $\dfrac{|Q_C|}{|Q_H|} = -\dfrac{Q_C}{Q_H} = \dfrac{T_C}{T_H}$ and $e = 1 - \dfrac{T_C}{T_H}$

A Steam engine operates at a boiler temperature of 450 K and an exhaust temperature of 300 K. What is the maximum theoretical efficiency of this system?

(a) 0.240

(b) 0.500

(c) 0.333

(d) 0.667

Using the environment as the cooler temperature bath, T_C, and having a finite T_H in which location would the Carnot engine be most efficient?

A. Summer in Anchorage, AK.

B. Summer in Nassau, Bahamas.

C. Winter in Anchorage, AK.

D. Winter in Nassau, Bahamas.