Module 4

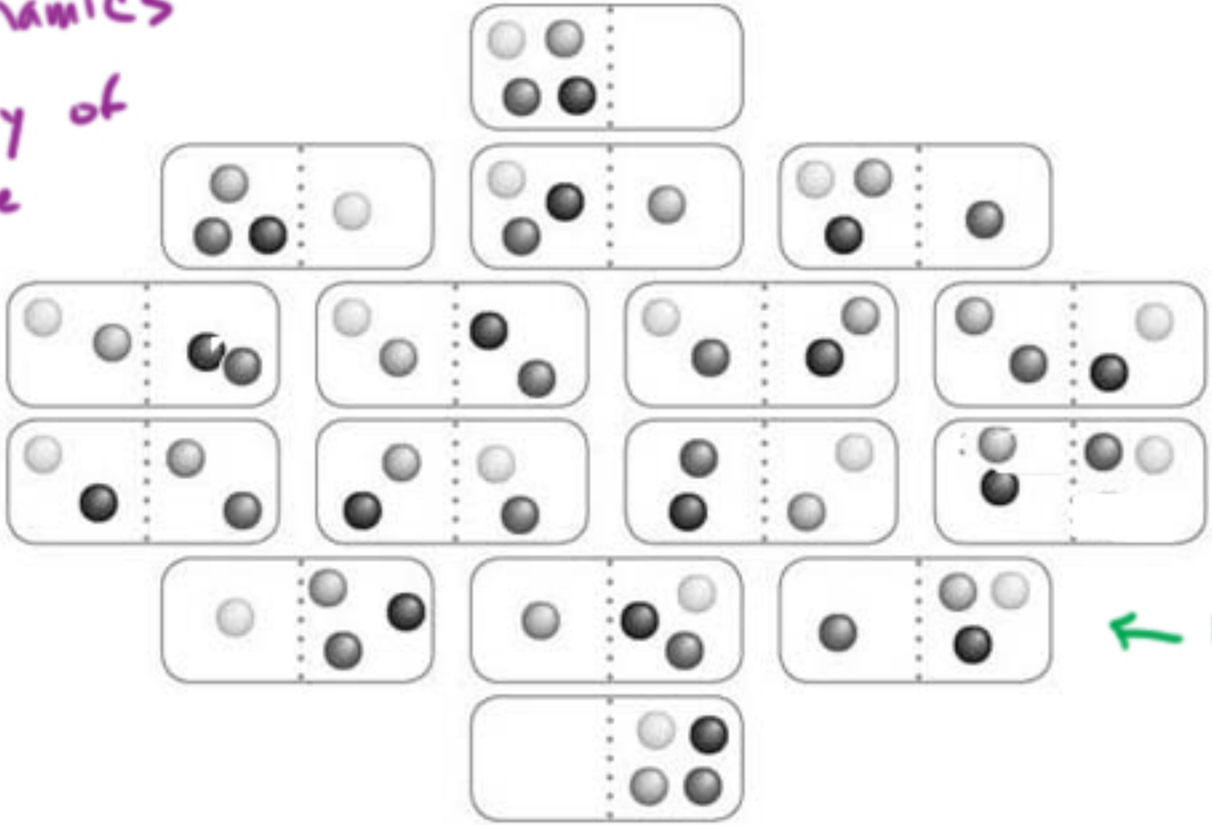
The Second Law of Thermodynamics

Session Slides with Notes

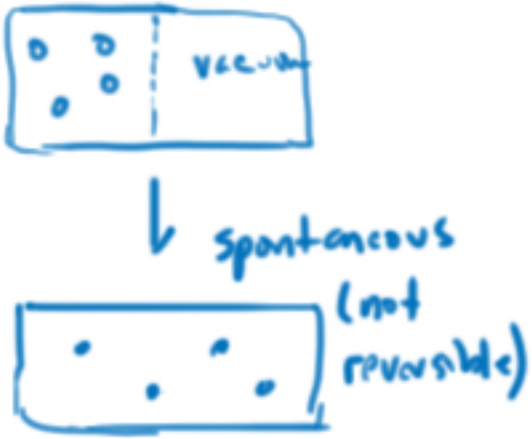
Entropy

2nd Law of Thermodynamics

The entropy of the universe always increases.



An isolated system tends toward disorder (greater entropy) because disordered states are more probable. Possible disordered states outnumber ordered states.



statistical ensemble of microstates

← microstates

$S = k \ln x$

multiplicity

- In the system below, two bulbs are connected by a tube and stopcock. In the initial state, all of the gas (N particles) is constrained to occupy a single bulb. When the stopcock is opened, the gas spontaneously moves to occupy both bulbs. In this example, with the stopcock opened, the probability of the second state is 2^N times that of the initial state.

adiabatic
free
expansion

- Entropy rises with the multiplicity of the system (the number of possible internal configurations that correspond to a particular macrostate).

$$S = k \ln X$$

S = entropy
k = Boltzmann's constant
X = multiplicity

Free expansion is an irreversible process in which a gas expands into an insulated evacuated chamber. During a free expansion

I. the temperature remains constant
II. the entropy of the gas increases
III. the internal energy of the gas remains constant

A. I
B. I and III
C. II and III
[✓ **D.**] I, II, and III

Carbon monoxide is a linear molecule. The carbon and oxygen atoms are roughly the same size and the dipole moment of the molecule is relatively small. This means that at temperatures just below its freezing point (74K), the molecules of this substance can flip easily in the crystal and assume one of two orientations with equal probability. The probability of flipping vanishes at even lower temperatures, though, as the temperature approaches absolute zero, where motion ceases and only one quantum energy state is available to each molecule. At absolute zero, the theoretical entropy of pure carbon monoxide crystal would be:

a. zero

[✓ b.] a small positive value

c. a small negative value

d. absolute zero is impossible to attain

$:C\equiv O:$

carbon monoxide

$C\equiv O \quad O\equiv C$

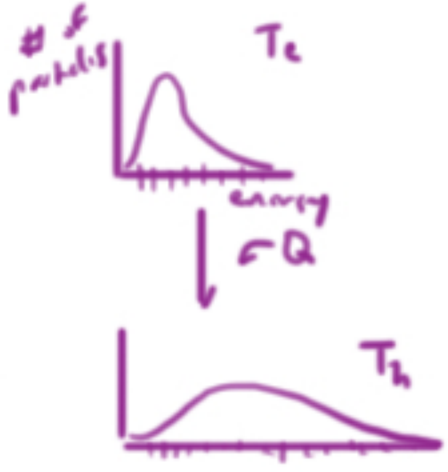
$C\equiv O \quad C\equiv O$

$O\equiv C \quad O\equiv C$

Entropy Change Due to Heat Flow

$$\Delta S = \frac{\Delta Q_r}{T}$$

ΔS = entropy change
Q_r = heat flow (in reversible process)
T = temperature



entropy lost
$\Delta S_H = \frac{Q}{T_H}$

entropy gained
$\Delta S_c = \frac{Q}{T_c}$

- entropy gained by the cold body is greater than what was lost by the hot body.
- entropy of the universe increased.

$\Delta S_{\text{universe}} \oplus$

When a hot stone is dropped into a cool water bath and heat flows from the stone into the bath

A. More entropy is lost in the stone than gained by the water.
B. More entropy is gained by the stone than lost by the water.
[✓ **C.**] Less entropy is lost by the stone than gained by the water.
D. The change in entropy in the stone is balanced by an equal and opposite change in entropy in the water.

$\Delta U = Q - W$

Which of the following does NOT change for a sample of ideal gas undergoing an adiabatic compression?

[✓ A.] entropy
~~B.~~ internal energy
~~C.~~ pressure
~~D.~~ volume

$Q = 0$

$\Delta U = -W$

isentropic

$\Delta S_{universe} = 0$

reversible

Which of the following does NOT change for a sample of ideal gas undergoing an isothermal compression?

~~A.~~ entropy
[✓ B.] internal energy
C. pressure
D. volume

$\Delta U = 0$

$Q = W$

ΔS_{system} loss Q/T_0

$\Delta S_{surroundings}$ gain Q/T_0

$\Delta S_{universe} = 0$ also reversible

A sealed container holds 1-L of hydrogen gas (H_2) at STP. A second sealed container holds 1-L of helium gas (He) at STP. Both containers are heated isochorically to 100°C. Which gas experiences the greatest change in entropy?

$\Delta V = 0$

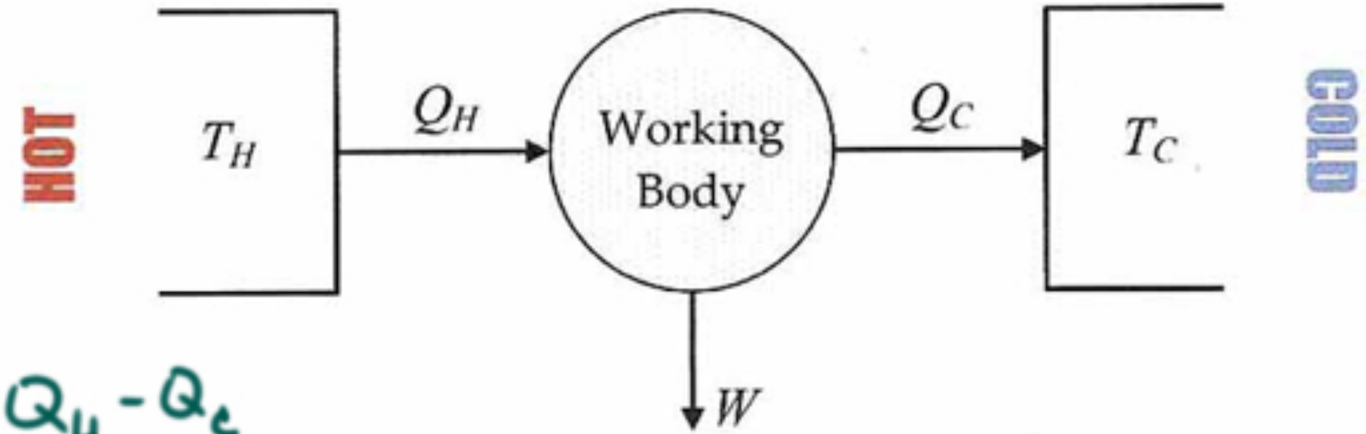
• same # of moles

- [✓ A.] the hydrogen gas
- B. the helium gas
- C. both have equal changes in entropy
- D. the entropy of neither gas changes

- How much of Q_H can we turn into work? thermal efficiency $\frac{W}{Q_H}$
- We know that we can turn none into work. That's spontaneous.
- Can we turn all of it into work? $\Delta S_H = \frac{Q_H}{T_H}$ ← hot body lost entropy

$\Delta S_{\text{universe}}$ would be $\ominus$

impossible



$W = Q_H - Q_c$

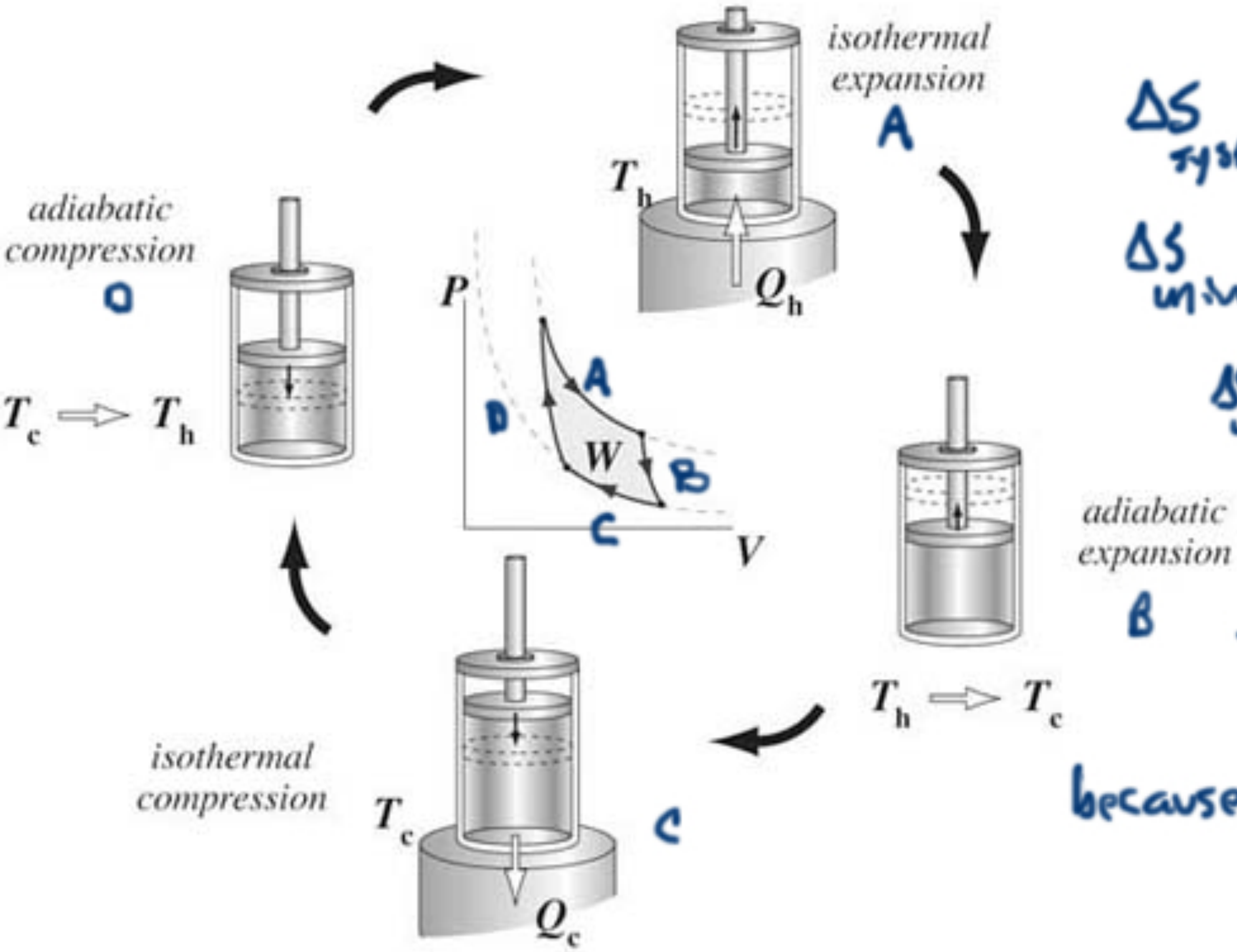
Best we can do is a reversible engine. $\frac{Q_H}{T_H} = \frac{Q_c}{T_c}$

combine equations: $\varepsilon = \frac{W}{Q_H} = 1 - \frac{T_c}{T_H}$

entropy lost = entropy gained

$\Delta S_{\text{universe}} = 0$

The Carnot Cycle



A Reversible Engine

$\Delta S_{system} = 0$ It's a cycle!

$\Delta S_{universe} = 0$ all stages are reversible

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$\Delta S_{surroundings} = 0$

therefore $\frac{Q_H}{T_H} = \frac{Q_c}{T_c}$

because $W = Q_H - Q_c$

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

$$\varepsilon = 1 - T_c/T_H$$

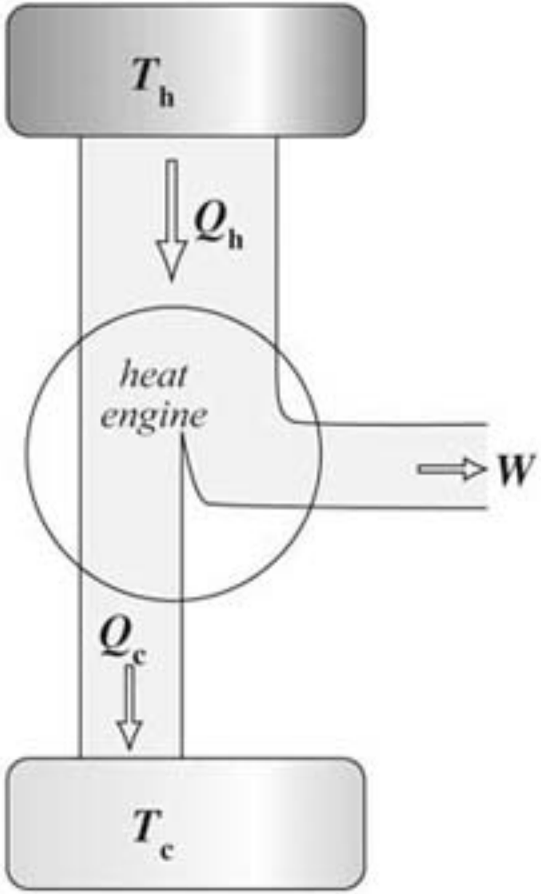
The Thermal Efficiency of a Heat Engine

$$\varepsilon = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

$$\varepsilon = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

(with heat input and output occuring at fixed temperatures)

ε = thermal efficiency
W = net work
Q_h = heat flow in
Q_c = heat flow out
T_h = hot sink temperature
T_c = cold sink temperature



Which of the following would tend to increase the thermal efficiency of the single stroke steam engine at right?

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

I. Increasing boiler temperature

II. Decreasing boiler temperature

III. Increasing condenser temperature

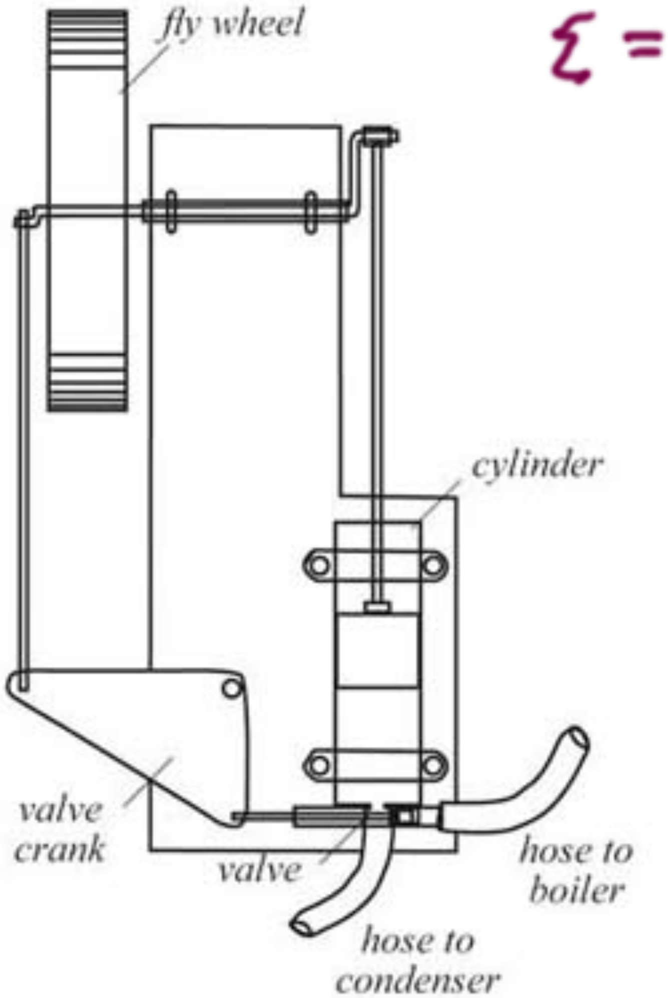
IV. Decreasing condenser temperature

a. I only

[✓ b.] I and IV

c. II only

d. II and III



What is the maximum efficiency of an engine operating between 177 °C and 27 °C?

[✓ A.] 33%
B. 85%
C. 50%
D. 15%

convert to Kelvin!

$$\varepsilon = 1 - \frac{T_C}{T_H}$$

$$= 1 - \frac{300\,K}{450\,K}$$

$$= 33\%$$

Coefficient of Performance

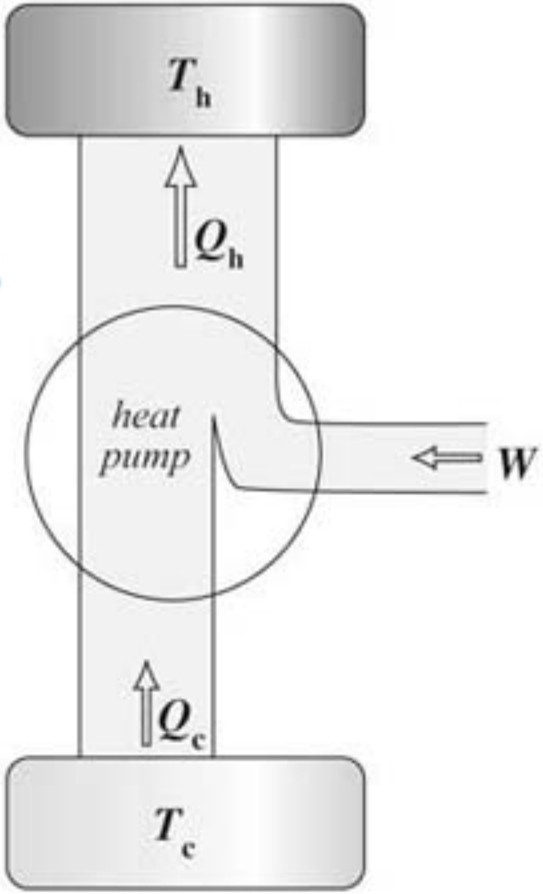
$$\mathrm{COP} = \frac{Q_h}{W}$$

$$= \frac{T_h}{T_h - T_c}$$

$$\frac{300\,K}{300\,K - 270\,K}$$

$$= 10$$

(with heat input and output occuring at fixed temperatures)

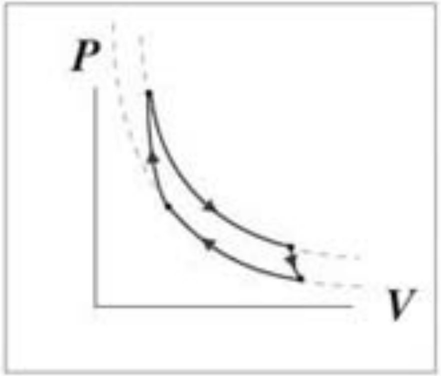


ε = thermal efficiency
W = net work
Q_h = heat flow in
Q_c = heat flow out
T_h = hot sink temperature
T_c = cold sink temperature

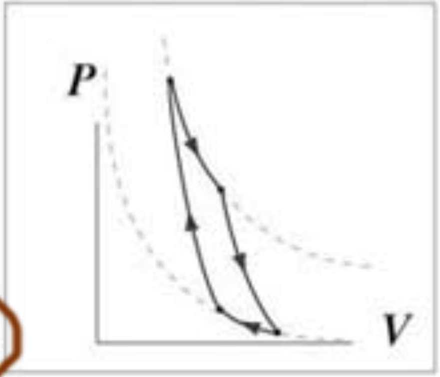
Which of the pressure-volume graphs below depicts the most efficient Carnot cycle?

$$\varepsilon = 1 - \frac{T_c}{T_H}$$

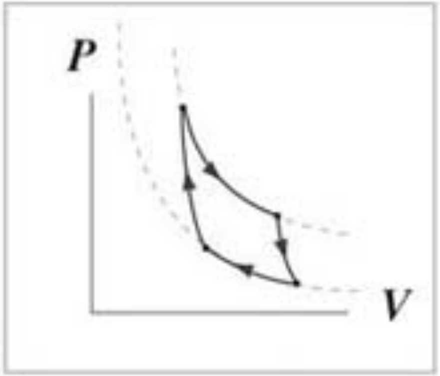
a.



[✓ b.]



c.

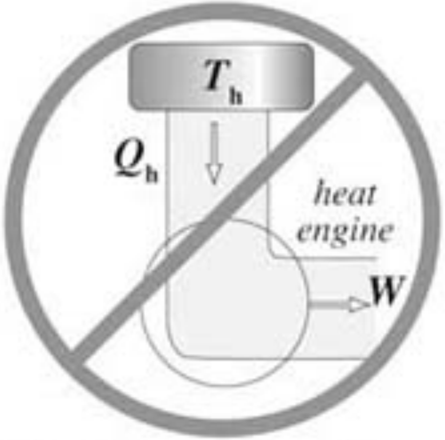


d. All three are equally efficient.

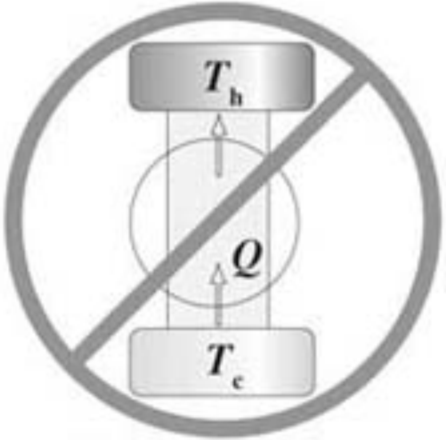
The Second Law of Thermodynamics

The entropy of the universe increases for all real processes.

No heat engine operating on a cycle can be 100% efficient (Kelvin's formulation).



Kelvin's formulation of the second law of thermodynamics



Clausius' formulation

An engine cannot transfer heat continuously from a colder to a hotter body and produce no other effects (Clausius' formulation).