# The Second Law Of Thermodynamic

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# Work to compress irreversibly

- the work done by the surroundings can be calculated:

$$W_{surr} = p_{surr}(V_o - V_f) + mg\,(V_o - V_f)/A$$

- Force balance on final state: $p_f = p_{surr} = mg/A$
- Combine:

$$W_{surr} = -\,p_f\,(V_o - V_f) = -\,p_f V_f (V_o/V_f - 1) = -nRT\,(V_o/V_f - 1)$$

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- For $V_o/V_f = 3$

$$\frac{W_{rev}}{W_{irr}} = \frac{\ln(V_o / V_f)}{V_o / V_f - 1} = \frac{\ln 3}{3 - 1} = 0.55$$

- **The surroundings do less work in the reversible than in the irreversible process**

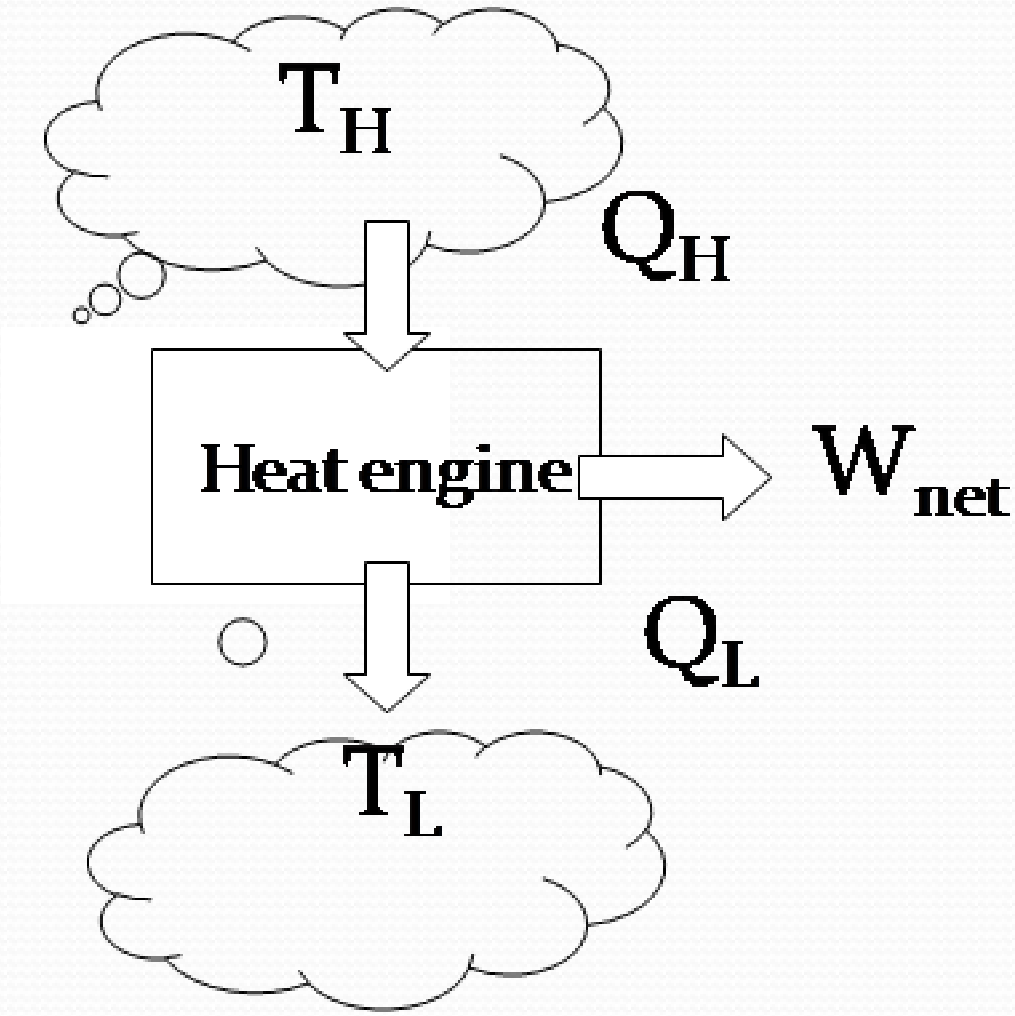
# Second Law of Thermodynamics

- Identify the direction of a process.
  (ex: Heat can only transfer from a hot object to a cold object, not the other around)
- Can be used to determine the "Quality" of the energy.
  (ex: A high-temperature energy source has a higher quality since it is easier to extract energy from it to deliver useable work.)
- Can be used to exclude the possibilities of constructing 100% efficient heat engine and any perpetual-motion machines. (Kevin-Planck statement and Clausius statement)
- Reversible processes and irreversibilities.
- Determine the theoretical limits for the performance of engineering systems. (ex: A Carnot engine is theoretically the most efficient heat engine and its performance can be used to set as a standard for other practical machines)

# Second Law-cont.

- A process can not happen unless it satisfies both the first and second laws of thermodynamics. The first law characterizes the balance of energy which defines the "quantity" of energy. The second law defines the direction which the process can take place and its "quality".

- Define a "Heat Engine": A device that converts heat energy into work while operating in a cycle. Ex: A steam power plant.




$\Delta Q - W_{net} = \Delta U$, $\Delta U = 0$ for a cycle

$W_{net} = Q_H - Q_L$

Thermal efficiency

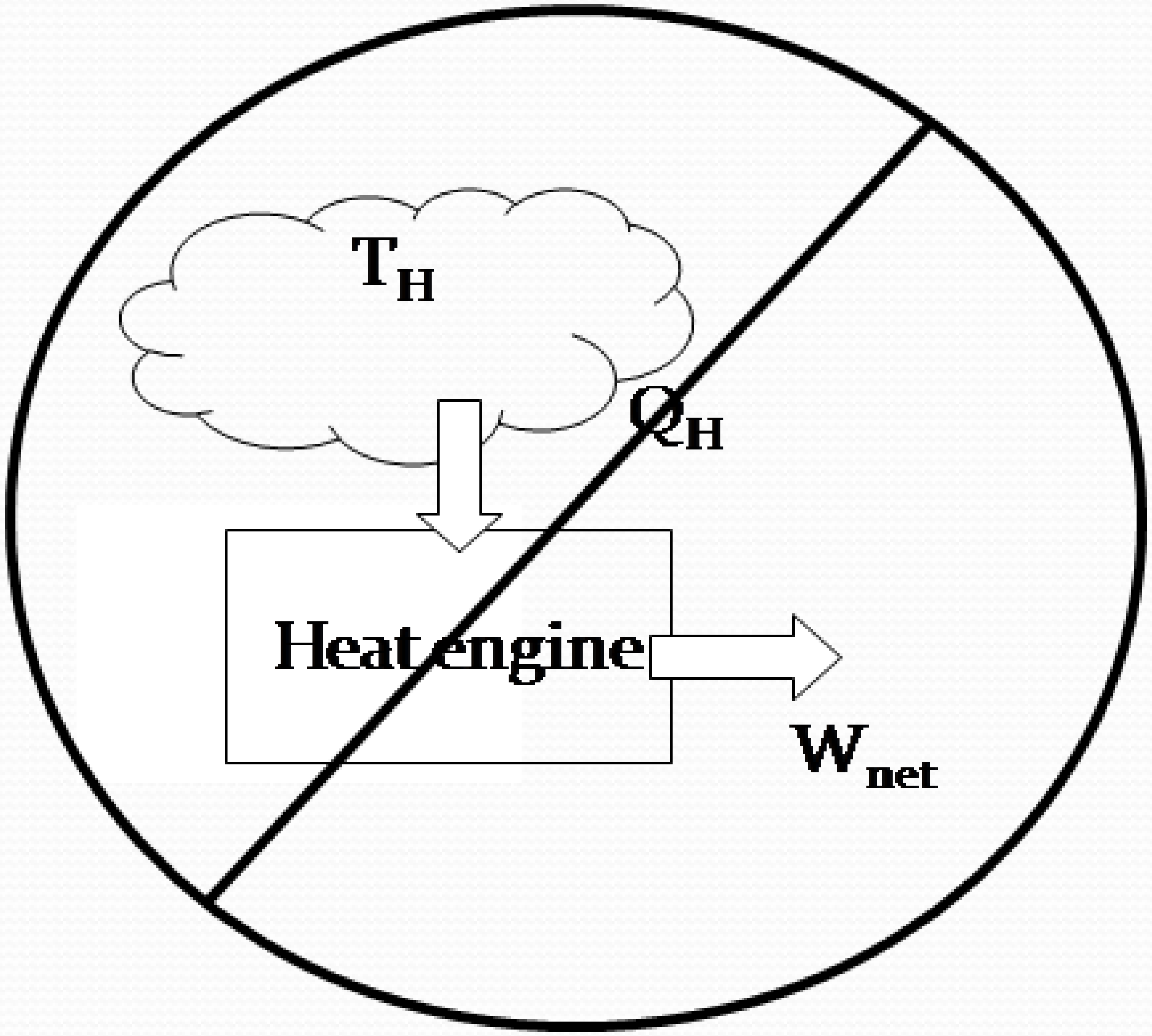
$\eta_{th} = W_{net}/Q_H = (Q_H - Q_L)/Q_H$

$= 1 - (Q_L/Q_H)$

Question: Can we produce an 100% heat engine? $Q_L = 0$?

# Kevin-Planck Statement

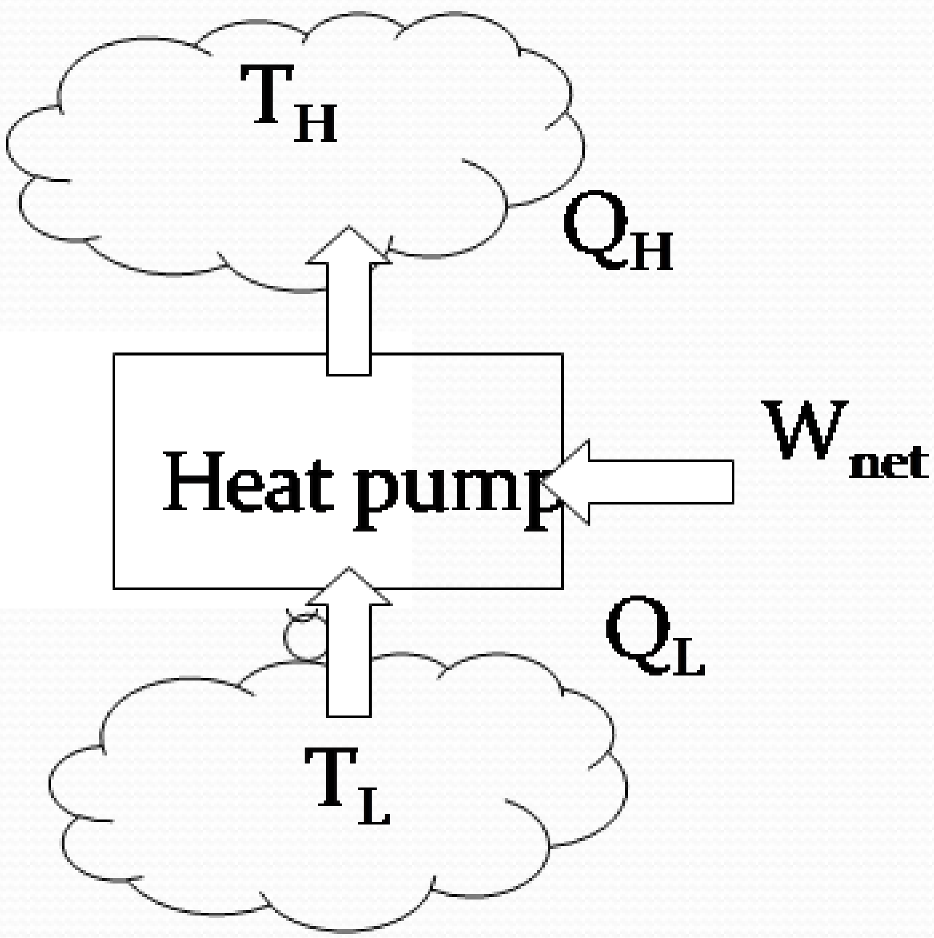
- It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produces a net amount of work.
- This is a statement without proof, but has not been disproved yet.
- Therefore, the question from previous slide is "NO". It is not possible to built a heat engine that is 100%.




- A heat engine has to reject some energy into a lower temperature sink in order to complete the cycle.
- $T_H > T_L$ in order to operate the engine. Therefore, the higher the temperature, the higher the quality of the energy source since it can produce useable work to more lower-temperature energy sinks.

# Heat Pump

• A "heat pump" is defined as a device that transfers heat from a low-temperature source to a high-temperature one. Ex: a heat pump to extract energy from outside cold outdoor air into the warm indoors.




• Coefficient of Performance (COP):

$COP = Q_H/W_{net} = Q_H/(Q_H - Q_L)$

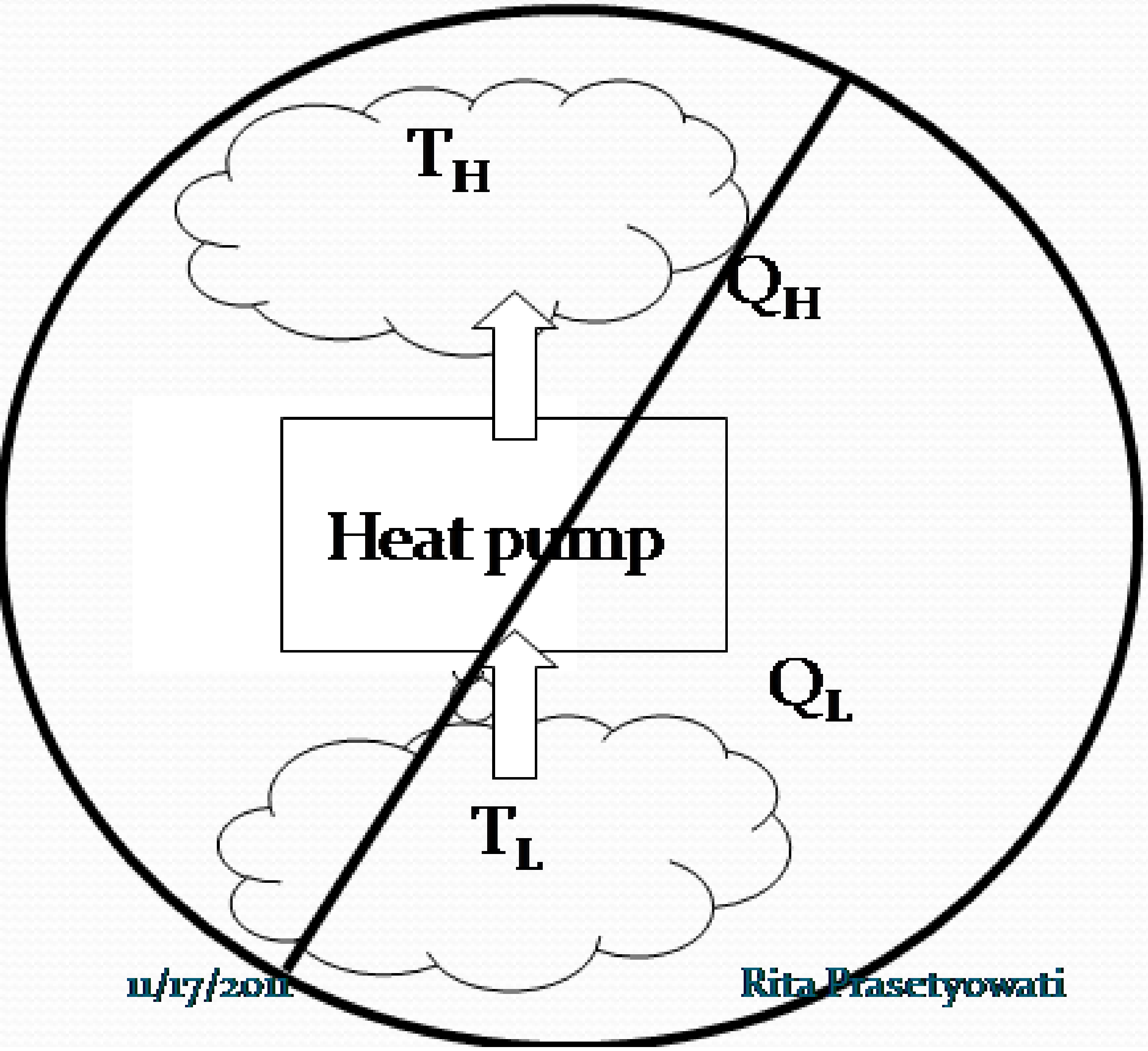
$= 1/(1-(Q_L/Q_H))$

• COP>1, ex: a typical heat pump has a COP in the order of 3

• Question: can we built a heat pump operating at ∞, that is $W_{net}=0$? $Q_H=Q_L$?

# Clausius Statement

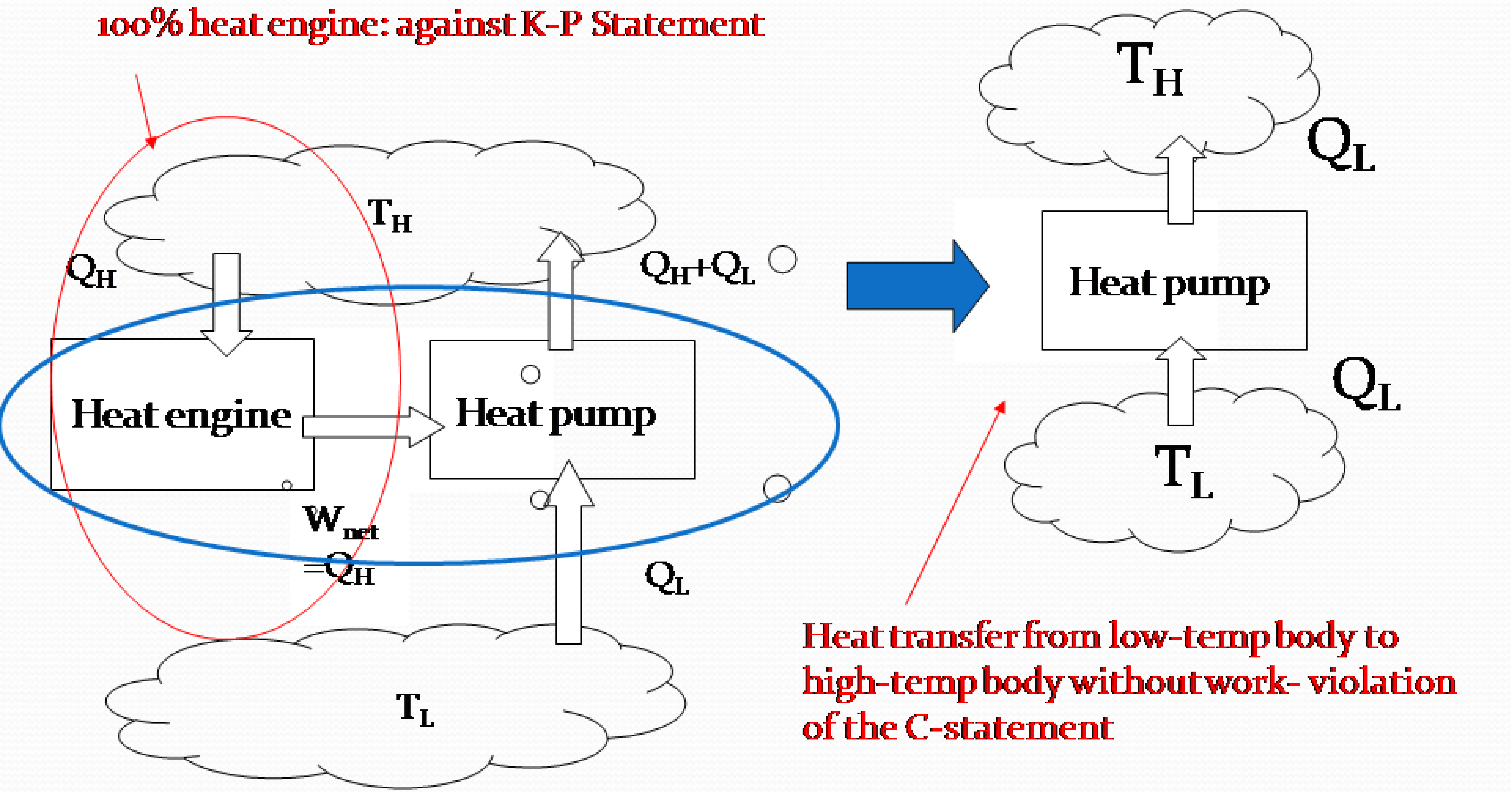
- It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.
- Also can not be proved, rather depends on experimental observations.
- Heat can not transfer from low temperature to higher temperature unless external work is added.




- Therefore, it is not possible to built a heat pump without external work input.

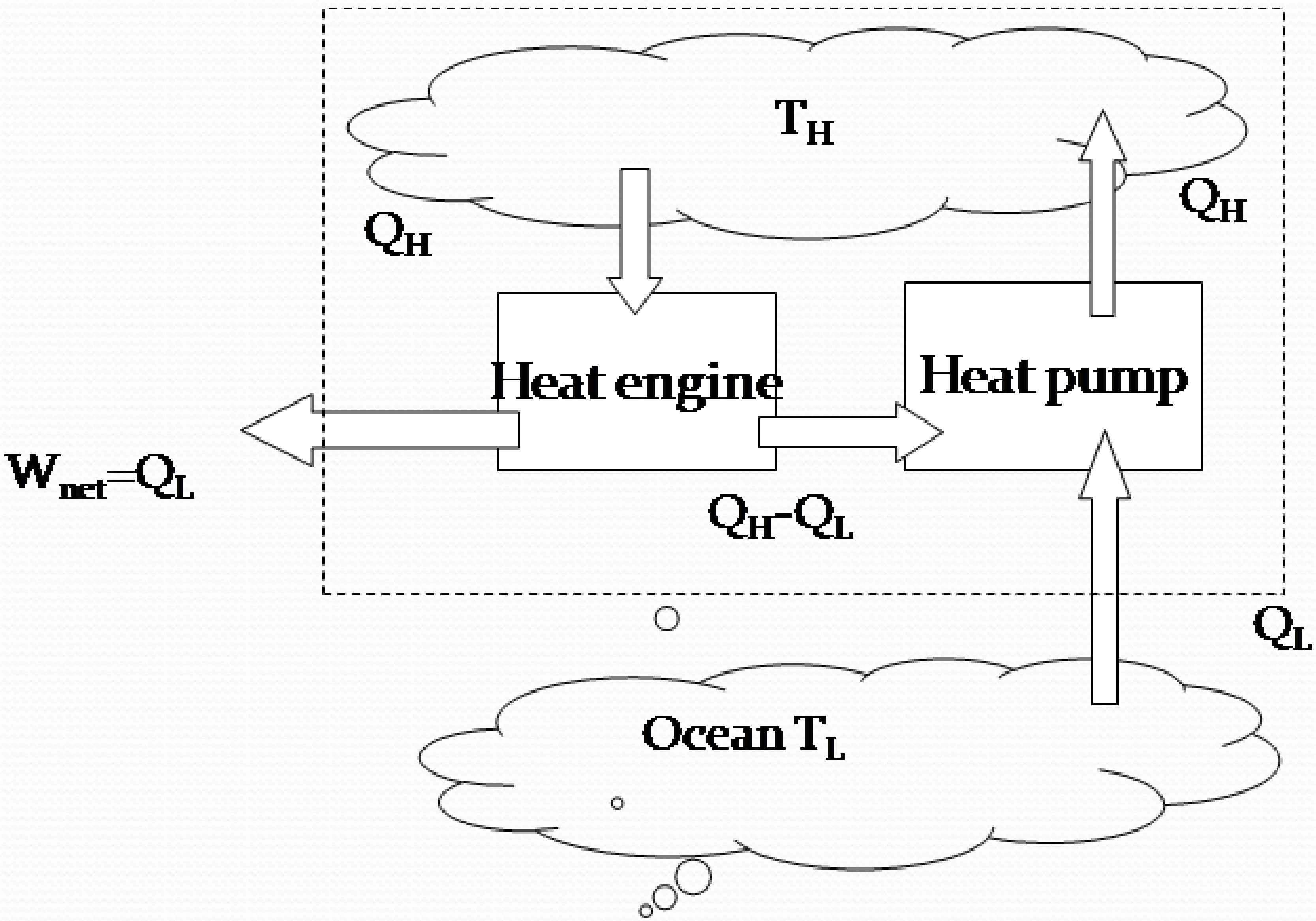
# Equivalence of the Two Statements

- It can be shown that the violation of the one statement means the violation of the other statement. They are equivalent.



# Perpetual-Motion Machine

Imagine that if we can extract energy from unlimited low-temperature energy sources such as the ocean or the atmosphere.




- It is against the Kevin-Planck statement: it is impossible to build an 100% heat engine.

# The Second Law of Thermodynamics

## *Clausius statement for refrigerator*

- **It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow. Energy will not flow spontaneously from a low temperature object to a higher temperature object.**
- The statements about refrigerators apply to air conditioners and heat pumps which embody the same principles.

# Second Law of Thermodynamics

- Statement: *"In all energy exchanges, if no energy enters or leaves the system, the potential energy of the state will always be less than that of the initial state.*"

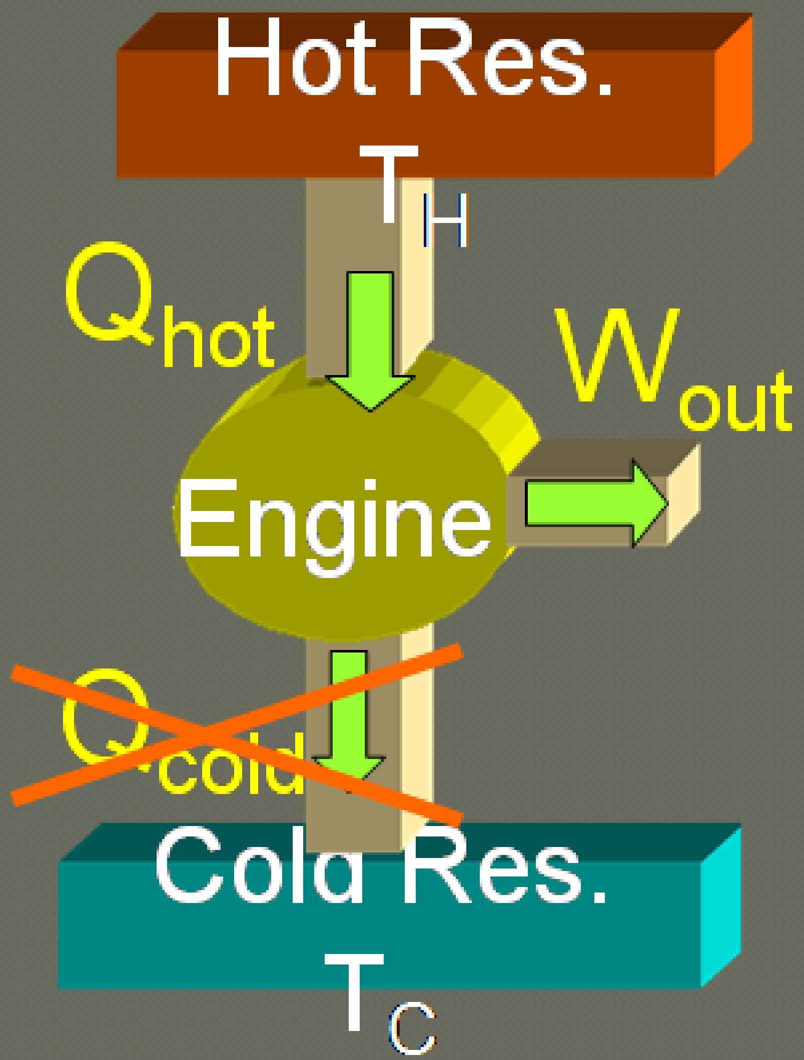
# The need for a new law : Which way will something go?

Many process occur spontaneously
(the reverse never happens unaided)

- ✓Ballons pop (and don't pop)
- ✓Iron rusts (and doesn't rusts)
- ✓Rivers flow downhill (never uphill)
- ✓Heat flows from a hotter objects to a colder one (never in the opposite direction)

The reverse off all these conserve energy so the first law is no use in predicting direction

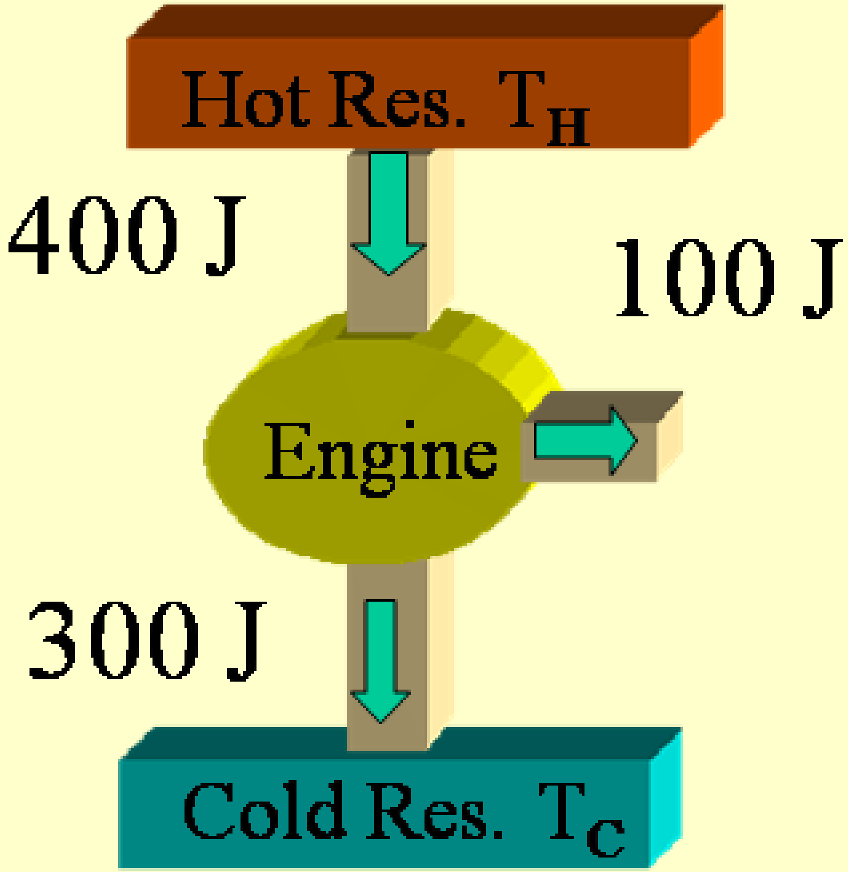
# THE SECOND LAW OF THERMODYNAMICS



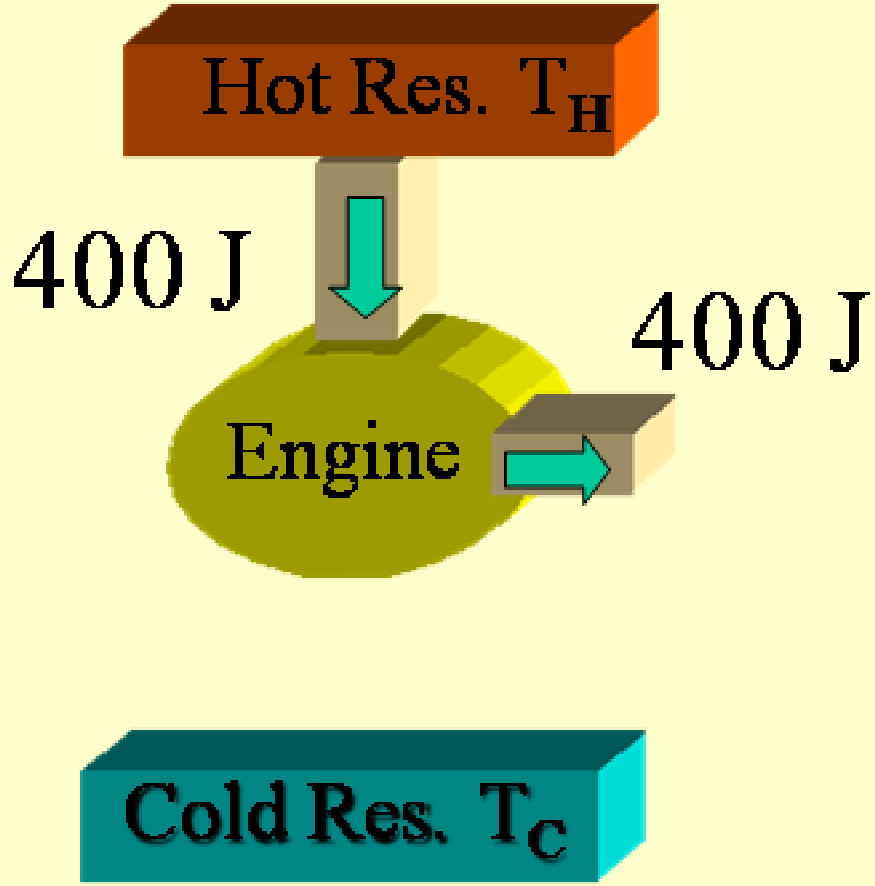

It is impossible to construct an engine that, operating in a cycle, produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Not only can you not win (1st law); you can't even break even (2nd law)!

# THE SECOND LAW OF THERMODYNAMICS

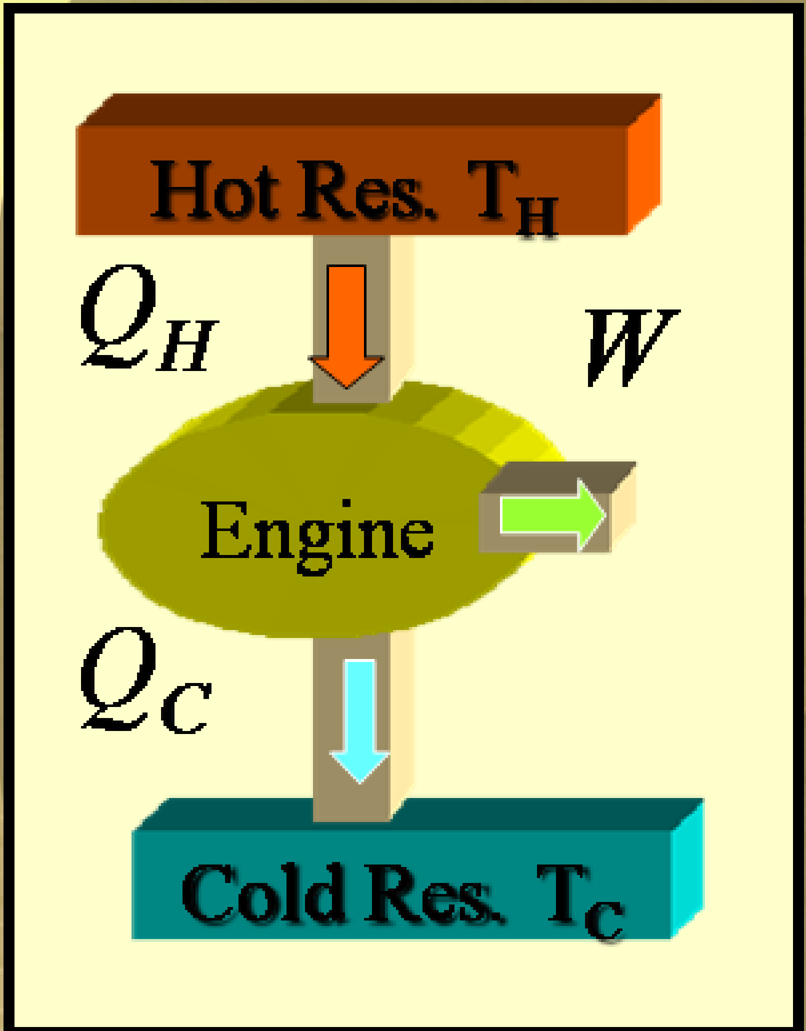



- A possible engine.




- An IMPOSSIBLE engine.

# EFFICIENCY OF AN ENGINE

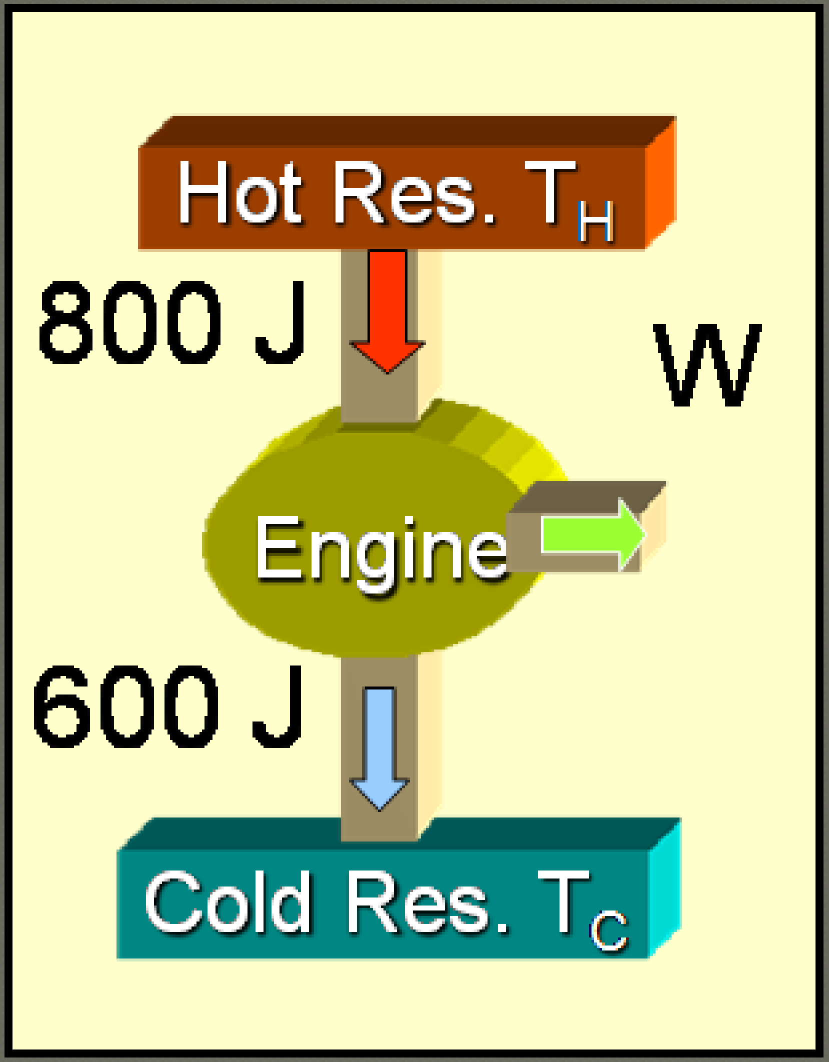



The efficiency of a heat engine is the ratio of the net work done W to the heat input $Q_H$.

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

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

# EFFICIENCY EXAMPLE




An engine absorbs 800 J and wastes 600 J every cycle. What is the efficiency?

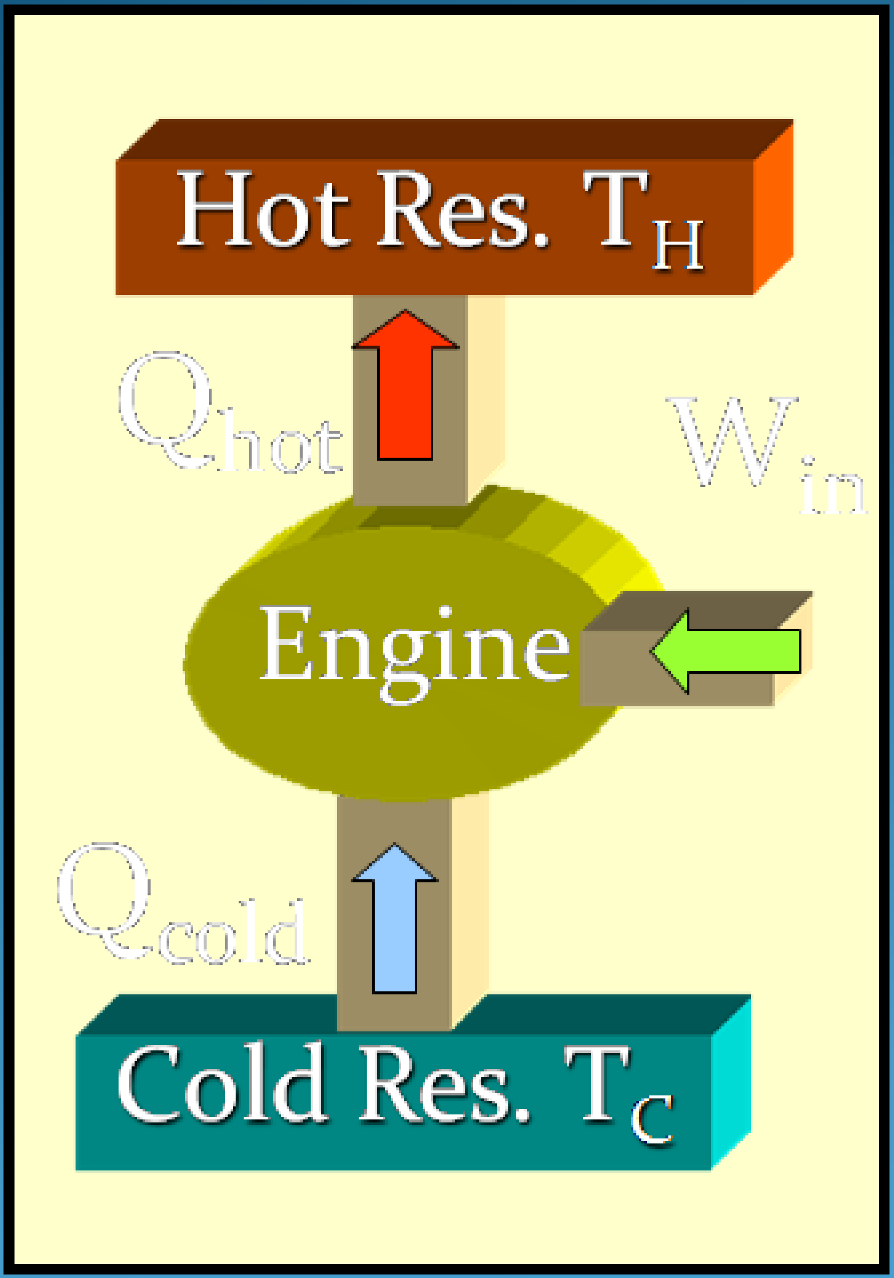
$$e = 1 - \frac{Q_C}{Q_H}$$

$$e = 1 - \frac{600\ J}{800\ J}$$

**e = 25%**

Question: How many joules of work is done?

# REFRIGERATORS

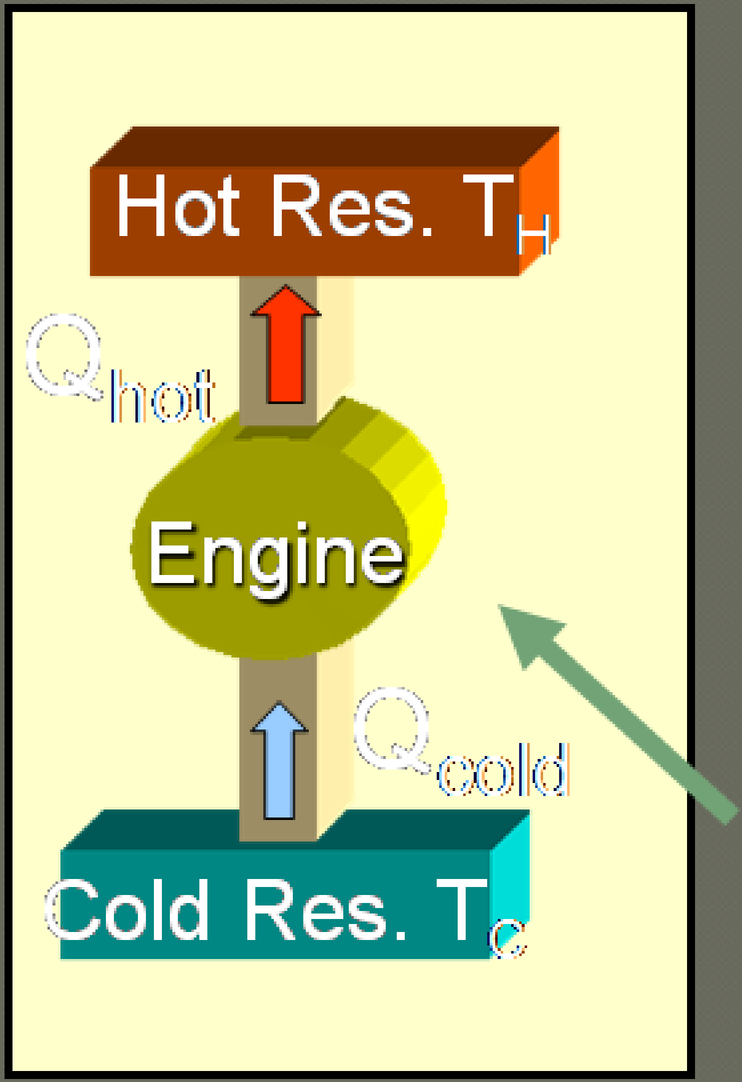



A refrigerator is an engine operating in reverse: Work is done on gas extracting heat from cold reservoir and depositing heat into hot reservoir.

$$W_{in} + Q_{cold} = Q_{hot}$$

$$W_{IN} = Q_{hot} - Q_{cold}$$

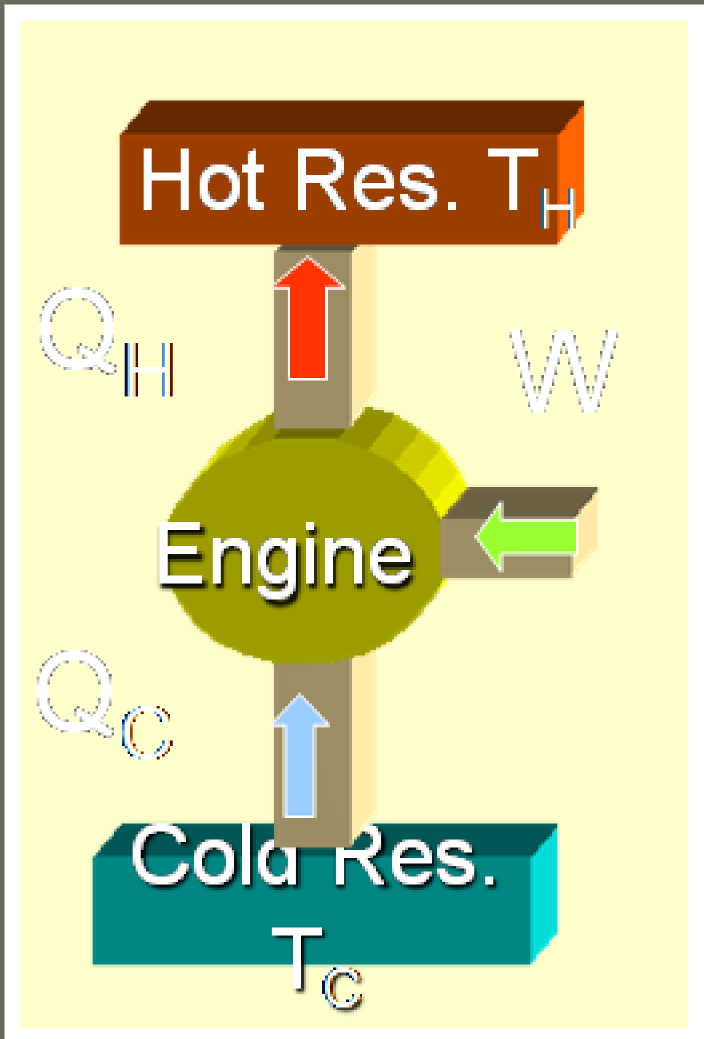
# THE SECOND LAW FOR REFRIGERATORS




It is impossible to construct a refrigerator that absorbs heat from a cold reservoir and deposits equal heat to a hot reservoir with $\Delta W = 0$.

If this were possible, we could establish perpetual motion!

# COEFFICIENT OF PERFORMANCE



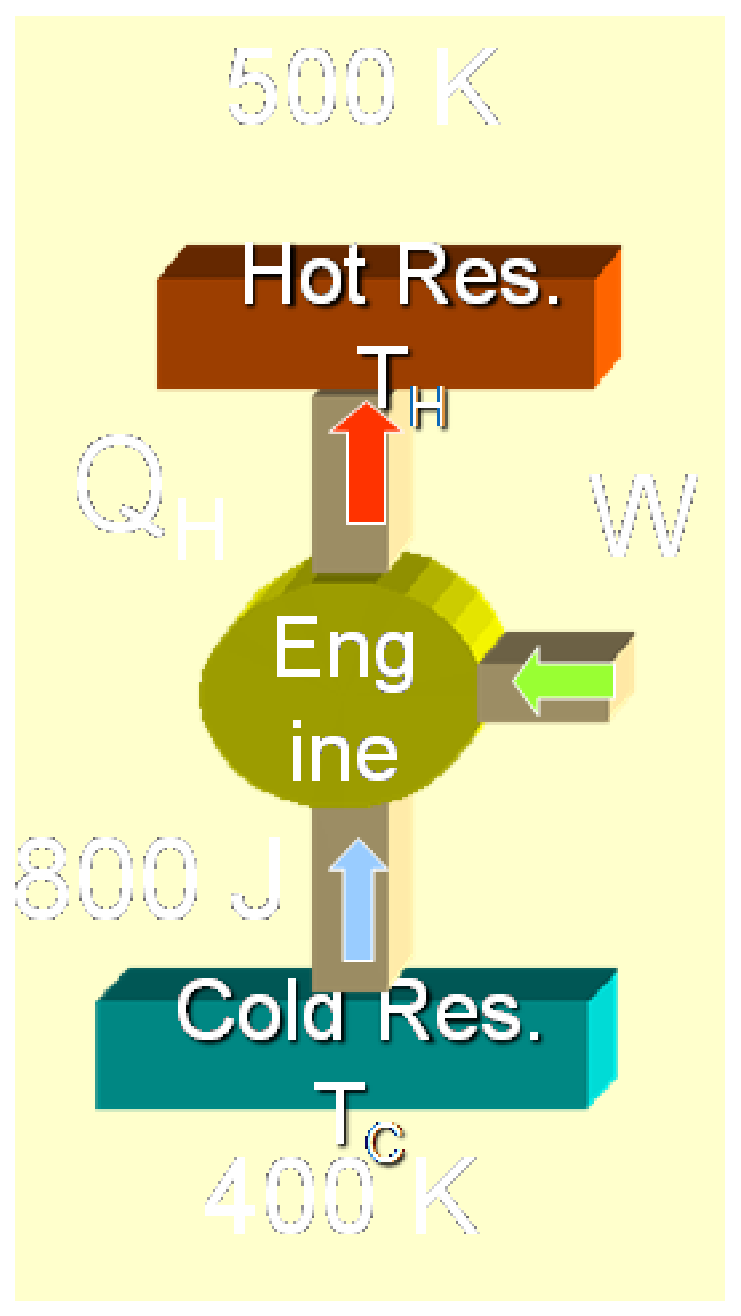

The COP (K) of a heat engine is the ratio of the HEAT $Q_H$ extracted to the net WORK done W.

$$K = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_C}$$

For an IDEAL refrigerator:

$$K = \frac{T_c}{T_H - T_C}$$

# COP EXAMPLE

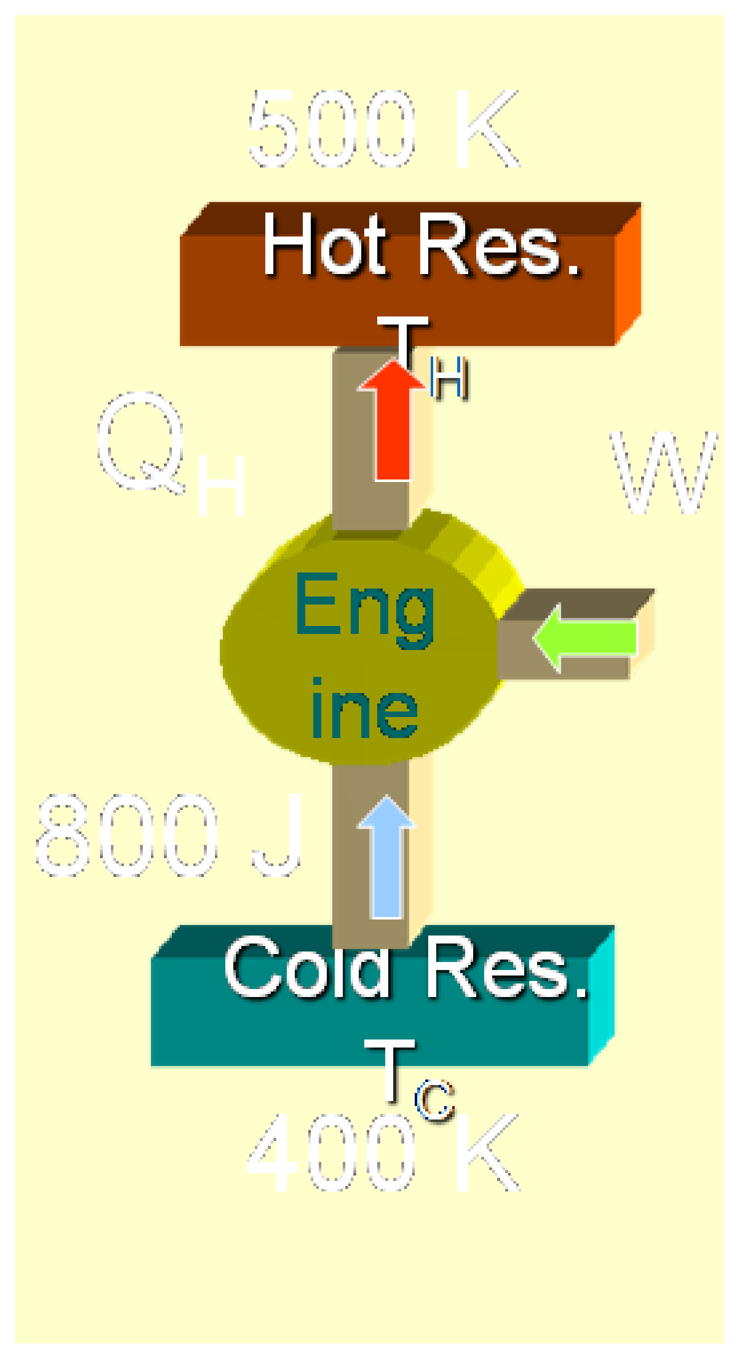



A Carnot refrigerator operates between 500 K and 400 K. It extracts 800 J from a cold reservoir during each cycle. What is C.O.P., W and $Q_H$ ?

$$K = \frac{T_C}{T_H - T_C} = \frac{400\text{ K}}{500\text{ K} - 400\text{ K}}$$

**C.O.P. (K) = 4.0**

# COP EXAMPLE (Cont.)



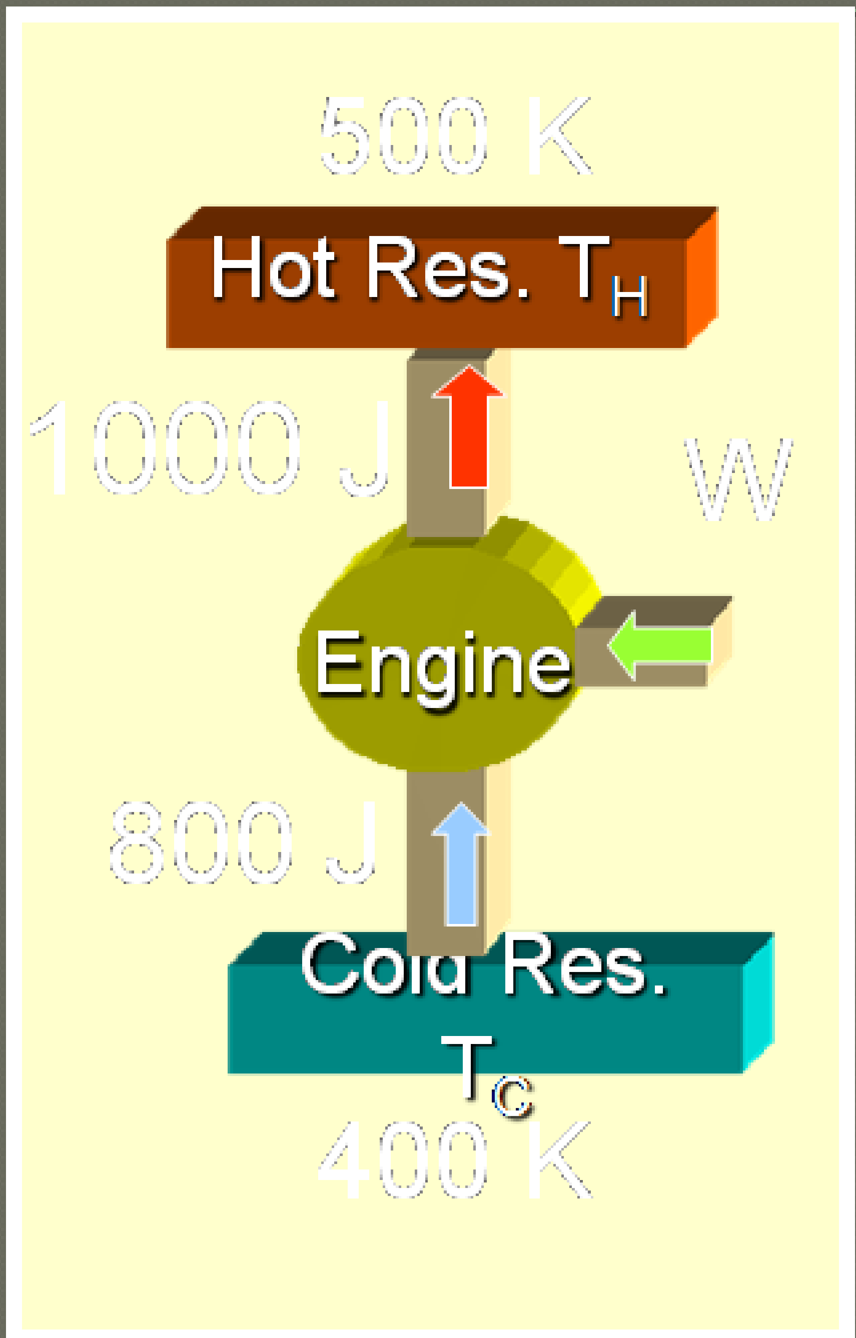

Next we will find $Q_H$ by assuming same K for actual refrigerator (Carnot).

$$K = \frac{Q_C}{Q_H - Q_C}$$

$$4.0 = \frac{800\ J}{Q_H - 800\ J}$$

$$Q_H = 1000\ J$$

# COP EXAMPLE (Cont.)




Now, can you say how much work is done in each cycle?

Work = 1000 J - 800 J

**Work = 200 J**

# Observation about the undirectionality of all naturally occuring processes

The direction of spontaneous change is always towards a state of equilibrium.

In order to drive a spontaneous process in the opposite direction (away from equilibirum) some external action is needed.

The method used to drive a process in the non-spontaneous direction always involves utilizing a different spontaneous process.

The combined process is spontaneous.

# Problems

1. A heat engine with 20.0% efficiency does 0.100 kJ of work during each cycle. (a) How much heat is absorbed from the hot reservoir during each cycle? (b) How much heat is released to the cold reservoir during each cycle?

As an engineer, you are designing a heat pump that is capable of delivering heat at the rate of 20 kW to a house. The house is located where, in January, the average outside temperature is –10°C. The temperature of the air in the air handler inside the house is to be 40°C. (a) What is maximum possible COP for a heat pump operating between these temperatures? (b) What must the minimum power of the electric motor driving the heat pump be? (c) In reality, the COP of the heat pump will be only 60 percent of the ideal value. What is the minimum power of the electric motor when the COP is 60 percent of the ideal value?

# Solution

**1. Solution**

**Picture the Problem** (*a*) The efficiency of the engine is defined to be $\varepsilon = W/Q_h$ where $W$ is the work done per cycle and $Q_h$ is the heat absorbed from the hot reservoir during each cycle. (*b*) Because, from conservation of energy, $Q_h = W + Q_c$, we can express the efficiency of the engine in terms of the heat $Q_c$ released to the cold reservoir during each cycle.

(*a*) $Q_h$ absorbed from the hot reservoir during each cycle is given by:

$$Q_h = \frac{W}{\varepsilon} = \frac{100\ \text{J}}{0.200} = \boxed{500\ \text{J}}$$

(*b*) Use $Q_h = W + Q_c$ to obtain:

$$Q_c = Q_h - W = 500\ \text{J} - 100\ \text{J} = \boxed{400\ \text{J}}$$

## 2. Solution

**Picture the Problem** We can use the definition of the $COP_{HP}$ and the Carnot efficiency of an engine to express the maximum efficiency of the refrigerator in terms of the reservoir temperatures. We can apply the definition of power to find the minimum power needed to run the heat pump.

(*a*) Express the $COP_{HP}$ in terms of $T_h$ and $T_c$:

$$COP_{HP} = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$$

$$= \frac{1}{1 - \frac{Q_c}{Q_h}} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c}$$

Substitute numerical values and evaluate $COP_{HP}$:

$$COP_{HP} = \frac{313\,K}{313\,K - 263\,K} = 6.26$$

$$= \boxed{6.3}$$

(*b*) The $COP_{HP}$ is also given by:

$$COP_{HP} = \frac{P_{out}}{P_{motor}} \Rightarrow P_{motor} = \frac{P_{out}}{COP_{HP}}$$

Substitute numerical values and evaluate $P_{motor}$:

$$P_{motor} = \frac{20\,kW}{6.26} = \boxed{3.2\,kW}$$

(*c*) The minimum power of the electric motor is given by:

$$P_{min} = \frac{\frac{dQ_c}{dt}}{\varepsilon_{HP}} = \frac{\frac{dQ_c}{dt}}{\varepsilon\left(COP_{HP,max}\right)}$$

where $\varepsilon_{HP}$ is the efficiency of the heat pump.

Substitute numerical values and evaluate $P_{min}$:

$$P_{min} = \frac{20\,kW}{(0.60)(6.26)} = \boxed{5.3\,kW}$$

Next Meeting :

**Carnot Cycle and Heat Kalor**

Some examples of spontaneous process

- Work changes into heat automatically;
- Gas inflates toward vacuum;
- Heat transfers from the high temp. object to the low temp. one;
- The solution of different concentration can mixed evenly;

➔The contrary process of these process can not proceed automatically. When it gets back to the original state by external force, the effect which can not be wore away will leave.

**Spontaneous process (change)**

Some changes have the trend of spontaneity, once happens, it can proceed automatically without the help of outside force.

**Common character**

Irreversible,

the contrary process of every spontaneous process is non-spontaneous.

# Reversible and Irreversibilities

- A reversible process means there are no irreversibilities exist when a system is undergoing interaction with its surroundings. Therefore, the process can be reversed without leaving any trace on its surroundings. Both system and the surroundings are returned to their initial states. It is an ideal process that can not happen in reality. However, if the irreversibilities are small enough, some processes can be approximated as reversible. Ex: a frictionless pendulum, quasi-equilibrium expansion and compression of gas in a cylinder/piston assembly (in an idealized Carnot cycle)

- Irreversibilities: friction, sudden expansion and compression, heat transfer between two bodies with finite temperature difference.

# Reversible Processes

- ***Internal:*** ***in the system***
- ***External:*** ***in the surroundings***
- Work done by the system is the same as the work done on the surroundings
- For the same initial and final states, work done reversibly is always > work done irreversibly
- Requirements of reversibility:

  - very slow; moves through equilibrium states

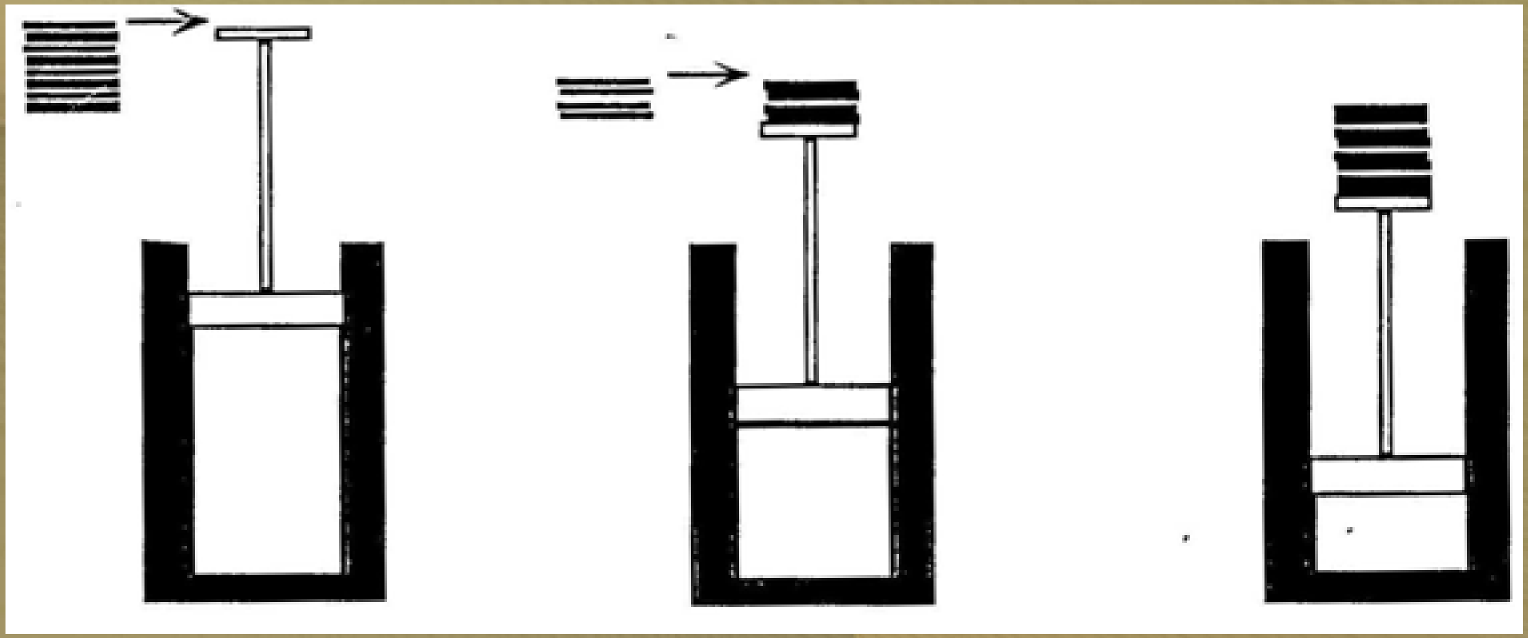
  - in fluids, no turbulence

  - no friction

  - infinitesimal $T - T_{surr}$ for heat; $p - p_{surr}$ for work

# Example: Reversible Isothermal compression of an ideal gas

Add small weights (total mass m) so that descent of piston is gentle; remove heat with very small $T - T_{surr}$



$$W_{rev} = \int_{V_0}^{V_f} p dV = nRT \int_{V_0}^{V_f} dV / V = -nRT \ln(V_o / V_f)$$

This is also $W_{surr}$, the work done *by* the surroundings

# Irreversible version

add single block of mass m; rapid descent;

violent bouncing of piston until final state reached

- Cannot integrate pdV