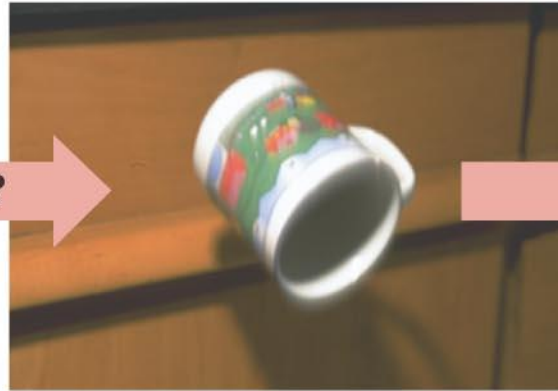


# **The Second Law of Thermodynamics**

# INTRODUCTION TO THE SECOND LAW



Initial state.

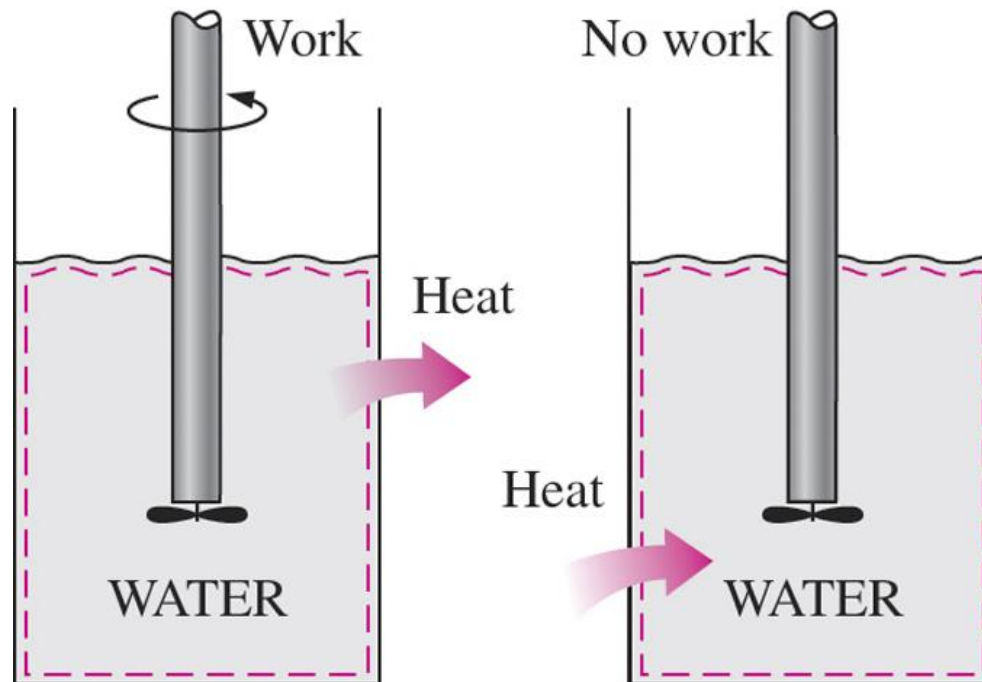


Later: cup reassembles and rises up.



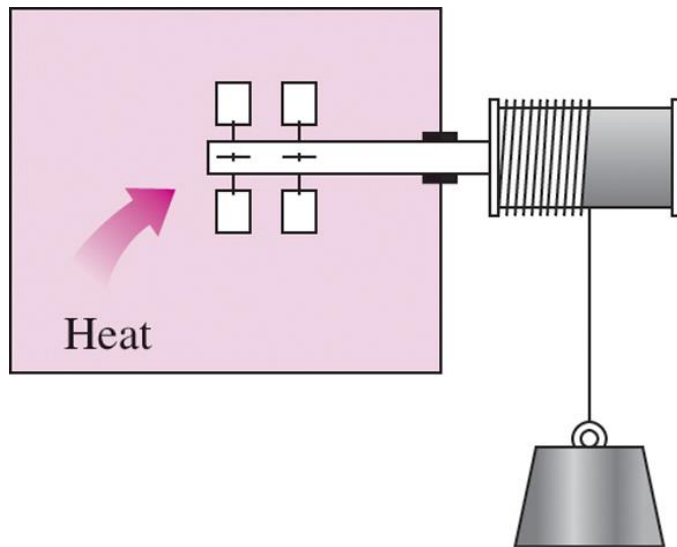
Later still: cup lands on table.

**The first law of thermodynamics tells us that energy is conserved. However, the absence of the process illustrated above indicates that conservation of energy is not the whole story. If it were, movies run backwards would look perfectly normal to us!**

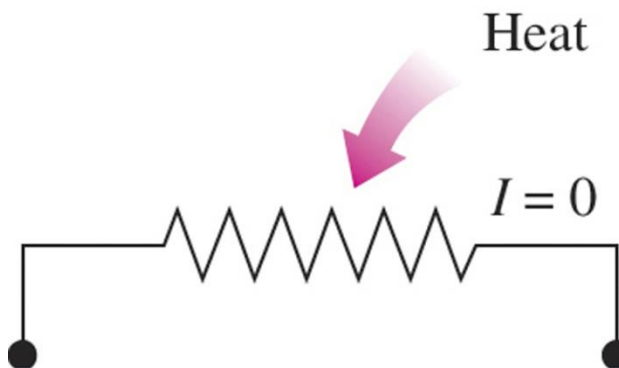


- ❖ Work can always be converted to heat directly and completely, but the reverse is not true

# INTRODUCTION TO THE SECOND LAW



Transferring heat to a paddle wheel will not cause it to rotate.



Transferring heat to a wire will not generate electricity.

These processes cannot occur even though they are not in violation of the first law.



Hot pans cool down when taken out from the stove.

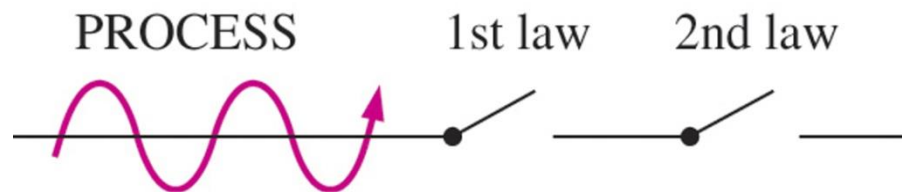


Ice cubes melt in a warm room.



Processes occur in a certain direction, and not in the reverse direction.

- ❖ The second law of thermodynamics enables us to determine the **feasibility of a process** and hence the **direction in which it will proceed**.

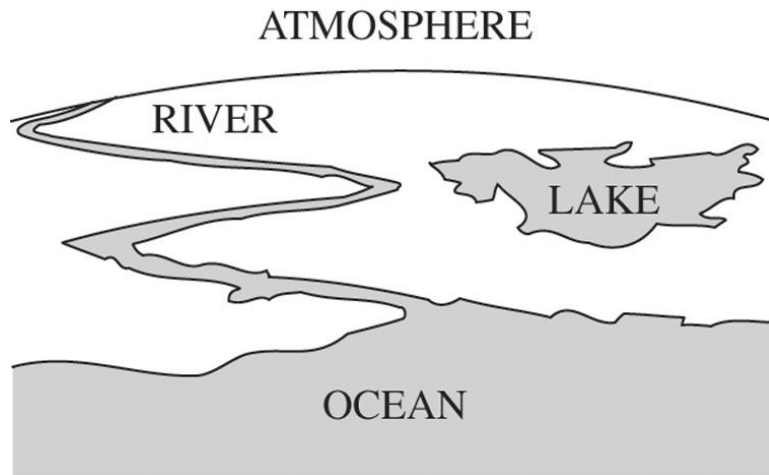


A process must satisfy both the first and second laws of thermodynamics to proceed.

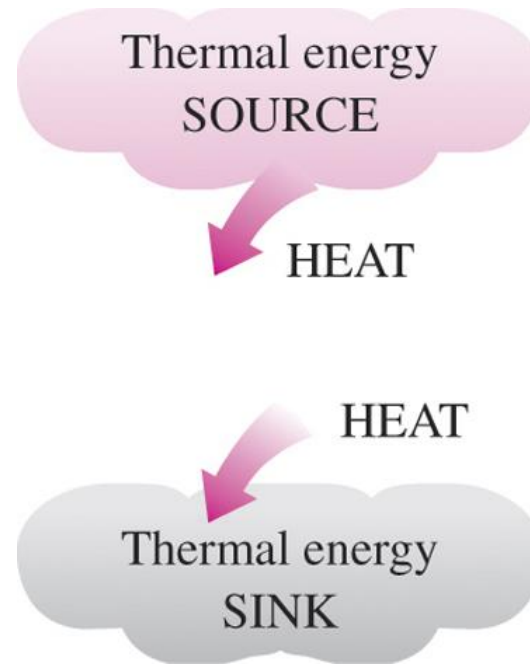
# MAJOR USES OF THE SECOND LAW

- The second law also asserts that energy has *quality* as well as quantity (e.g.: A high-temperature energy source has a higher quality since it is easier to extract energy from it to deliver useable work). The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality.
- The second law of thermodynamics is also used in determining the *theoretical limits* for the performance of commonly used engineering systems, such as heat engines and refrigerators (e.g.: A Carnot engine is theoretically the most efficient heat engine; its performance can be used as a standard for other practical engines)

# THERMAL ENERGY RESERVOIRS



Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

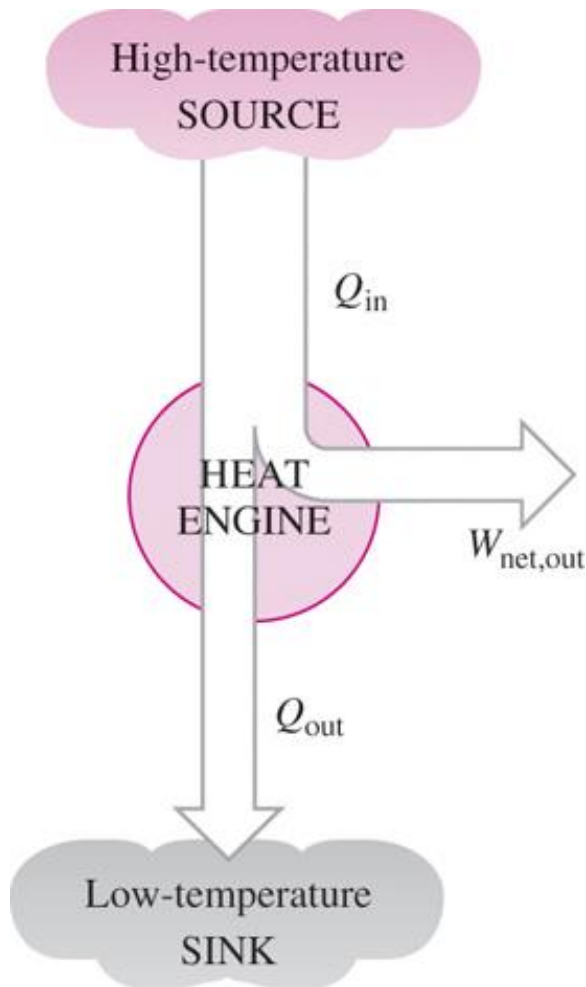


A source supplies energy in the form of heat, and a sink absorbs it.

- A hypothetical body with a relatively large *thermal energy capacity* ( $\text{mass} \times \text{specific heat}$ ) that can supply or absorb finite amounts of heat without undergoing any change in temperature is called a **thermal energy reservoir**, or just a reservoir.



# HEAT ENGINES



The devices that convert heat to work.

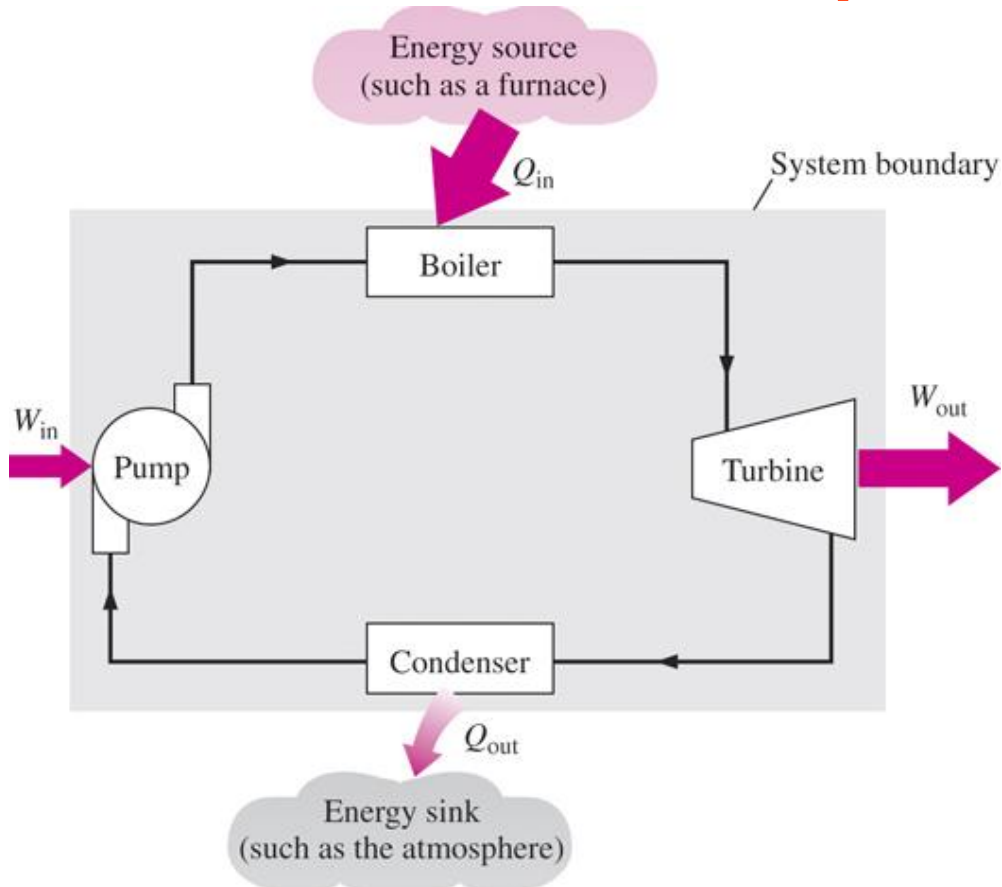
1. They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).

2. They convert part of this heat to work (usually in the form of a rotating shaft.)

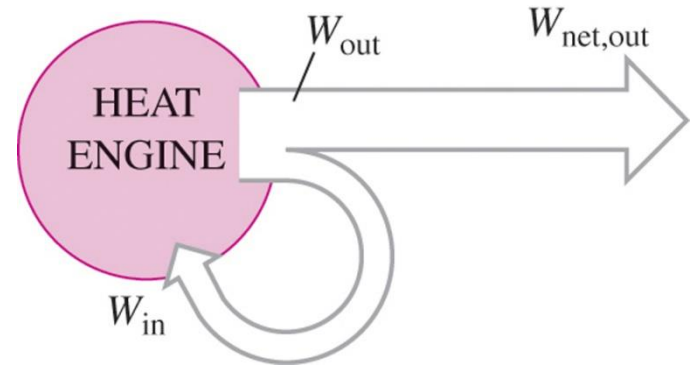
3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).

4. They operate on a cycle.

# A steam power plant



A portion of the work output of a heat engine is consumed internally to maintain continuous operation.



$$W_{net,out} = W_{out} - W_{in}$$

$$W_{net,out} = Q_{out} - Q_{in}$$

$Q_{in}$  = amount of heat supplied to steam in boiler from a high-temperature source (furnace)

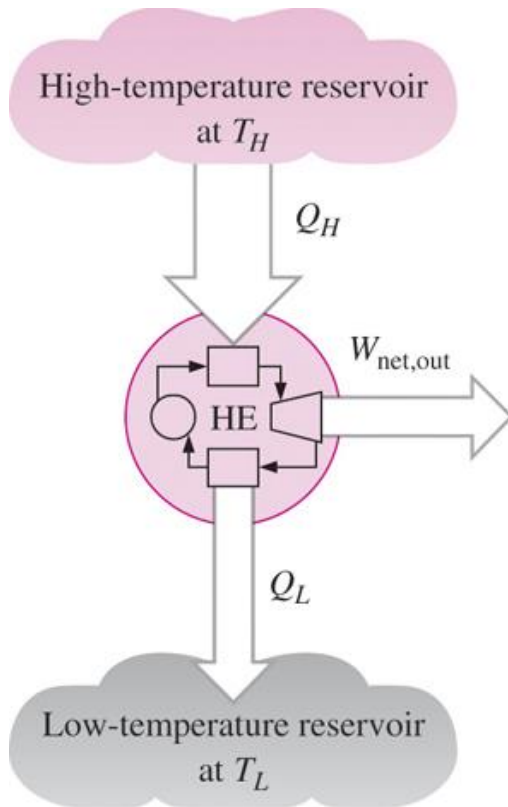
$Q_{out}$  = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)

$W_{out}$  = amount of work delivered by steam as it expands in turbine

$W_{in}$  = amount of work required to compress water to boiler pressure

# THERMAL EFFICIENCY

The efficiency of the heat engine is the ratio of the work done to the heat input:



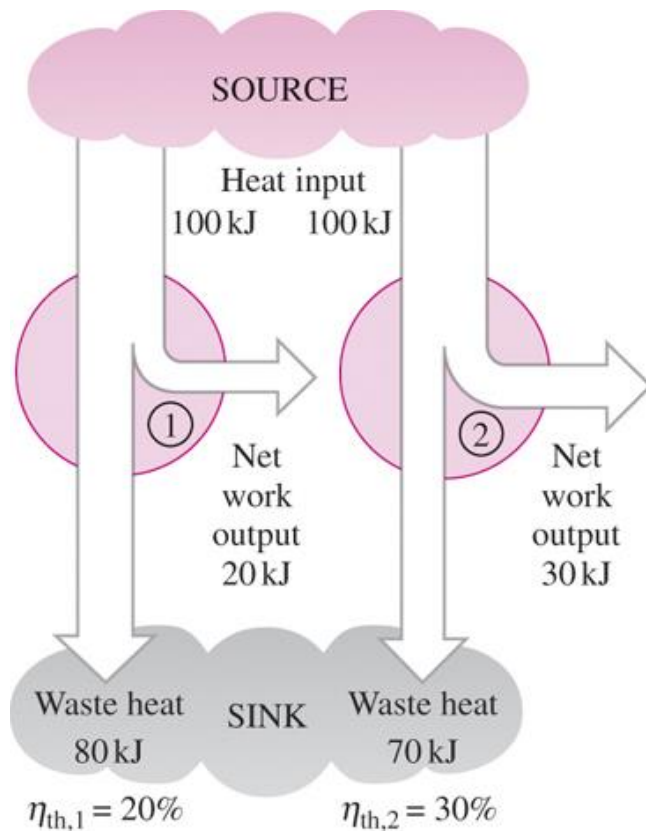
$$\eta_{th} = \frac{W_{net,out}}{Q_{in}}$$

$$\Rightarrow W_{net,out} = Q_H - Q_L$$

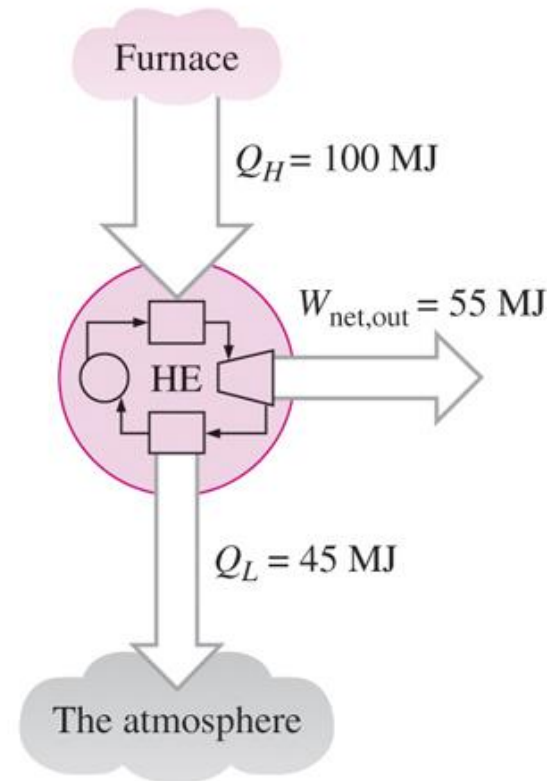
$$\Rightarrow \eta_{th} = \frac{Q_H - Q_L}{Q_H}$$

$$\Rightarrow \eta_{th} = 1 - \frac{Q_L}{Q_H}$$

# THERMAL EFFICIENCY



Some heat engines perform better than others (convert more of the heat they receive to work).



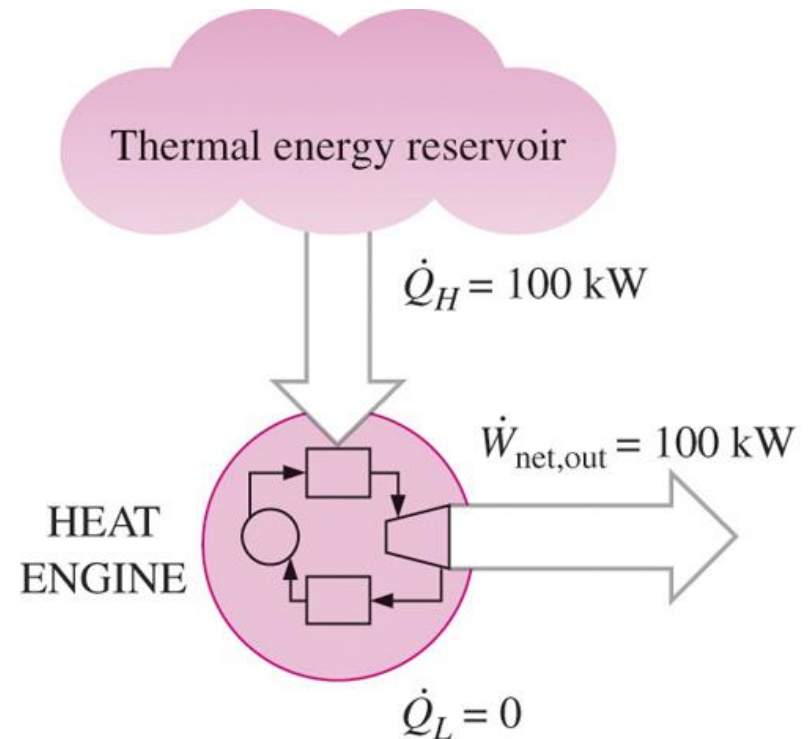
Even the most efficient heat engines reject almost one-half of the energy they receive as waste heat.

## The Second Law of Thermodynamics: Kelvin–Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work.

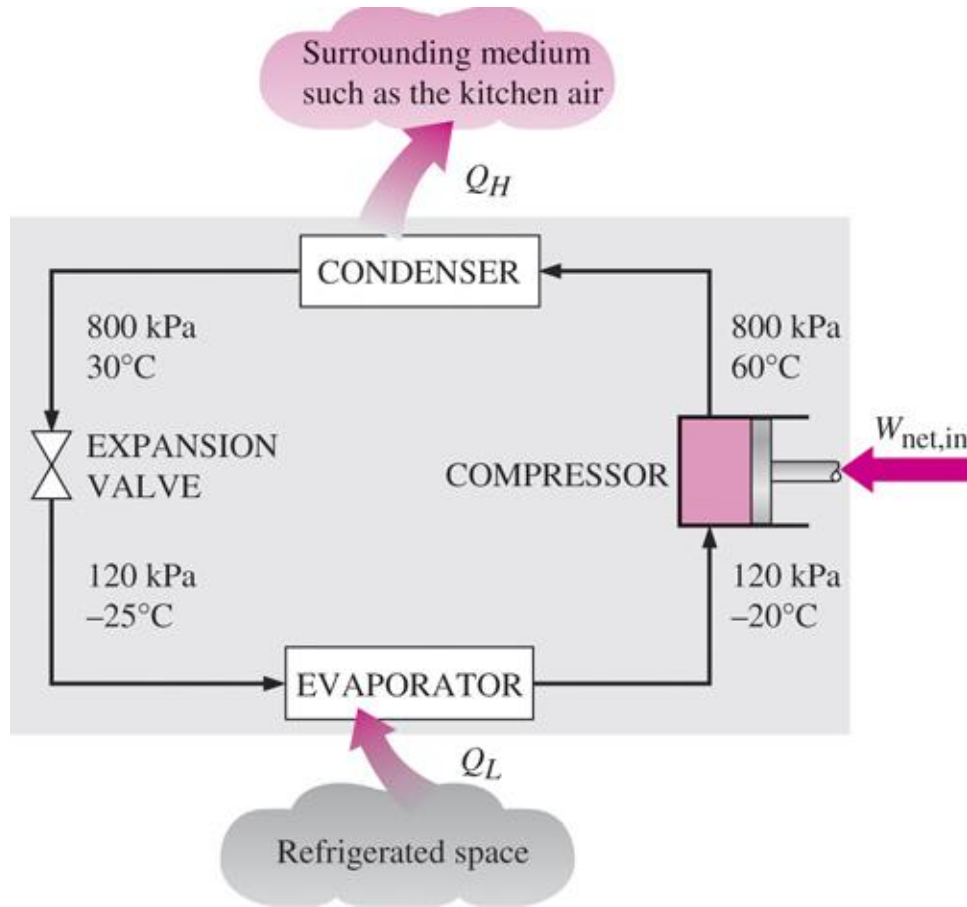
*No heat engine can have a thermal efficiency of 100 percent, or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.*

The impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.



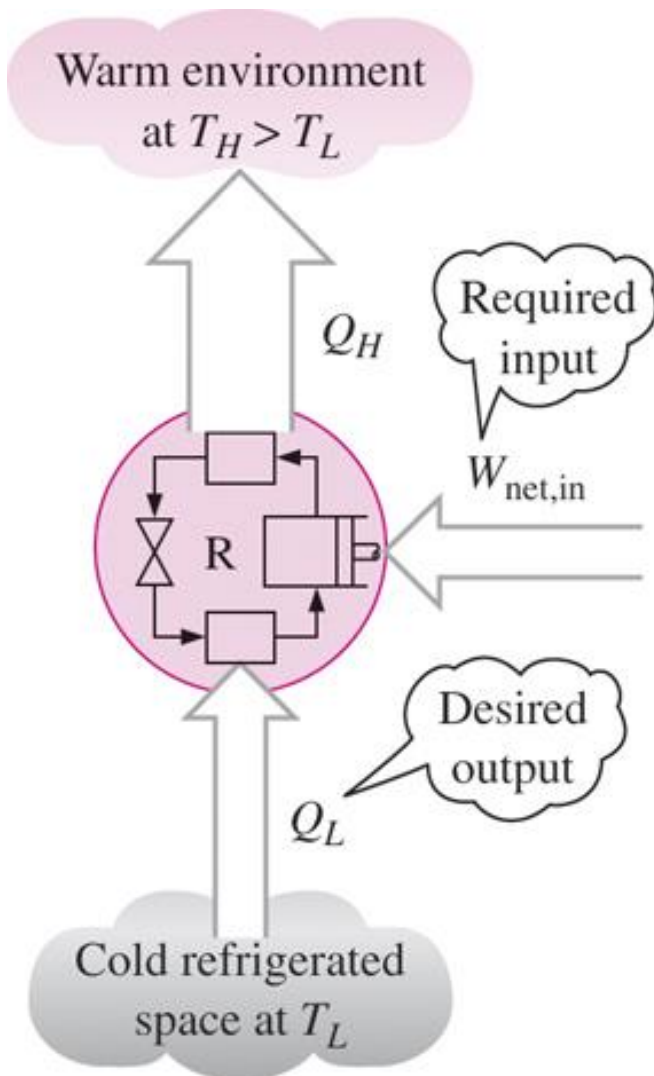
A heat engine that violates the Kelvin–Planck statement of the second law.

# REFRIGERATORS AND HEAT PUMPS



Basic components of a refrigeration system and typical operating conditions.

- The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called **refrigerators**.
- Refrigerators, like heat engines, are cyclic devices.
- The working fluid used in the refrigeration cycle is called a **refrigerant**.



## Coefficient of Performance

The *efficiency* of a refrigerator is expressed in terms of the **coefficient of performance** (COP).

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{net,in}}$$

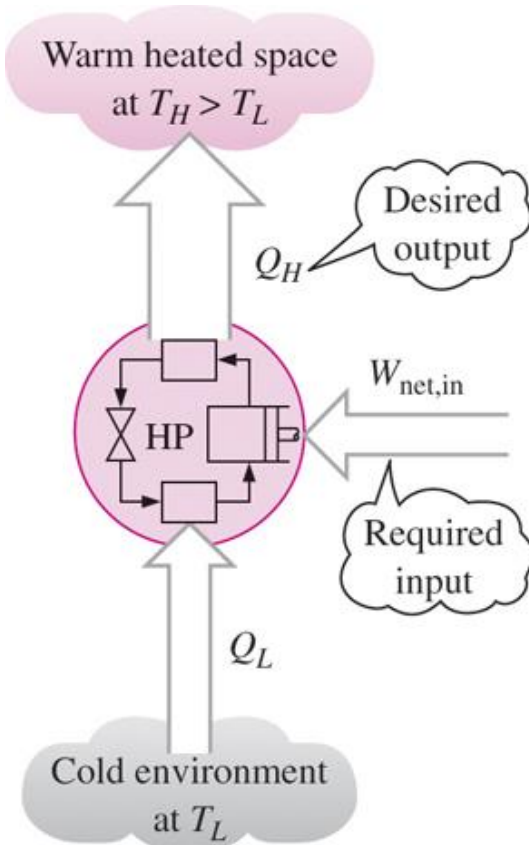
$$\Rightarrow W_{net,in} = Q_H - Q_L$$

$$COP_R = \frac{Q_L}{Q_H - Q_L}$$

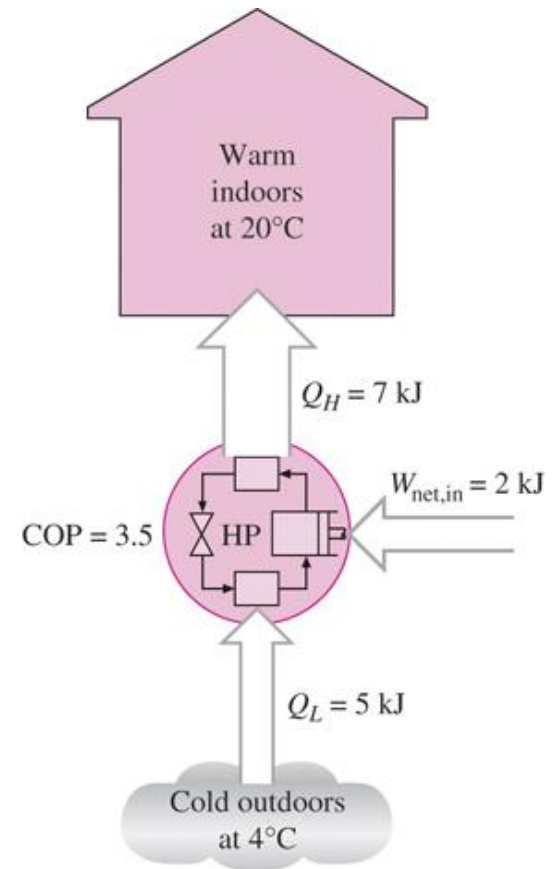
The objective of a refrigerator is to remove  $Q_L$  from the cooled space.

# Heat Pumps

The objective of a heat pump is to supply heat  $Q_H$  into the warmer space.



The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.



$$COP_{HP} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_H}{W_{net,in}}$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L}$$

$$\Rightarrow COP_{HP} = COP_R + 1 \quad \text{for fixed values of } Q_L \text{ and } Q_H$$



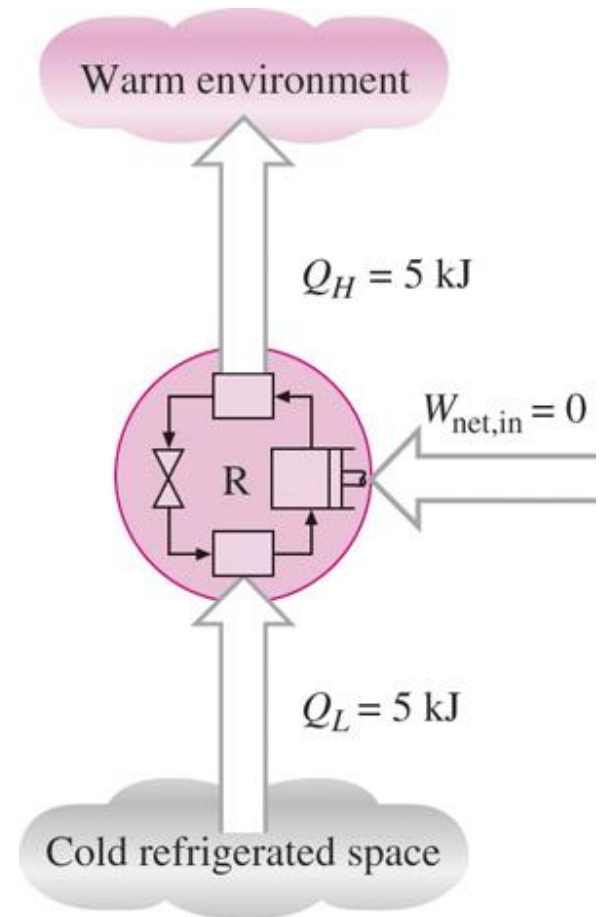
## The Second Law of Thermodynamics: Clausius Statement

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.

*It states that a refrigerator cannot operate unless its compressor is driven by an external power source, such as an electric motor.*

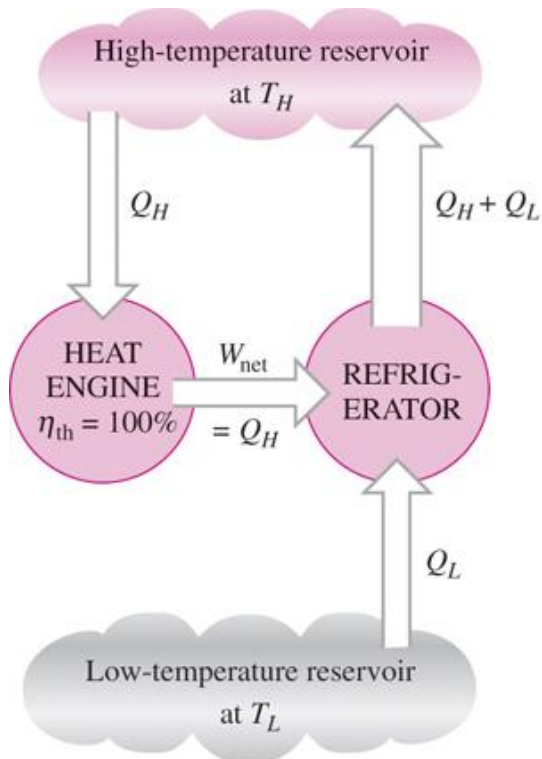
This way, the net effect on the surroundings involves the consumption of some energy in the form of work, in addition to the transfer of heat from a colder body to a warmer one.

To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient proof of its validity.

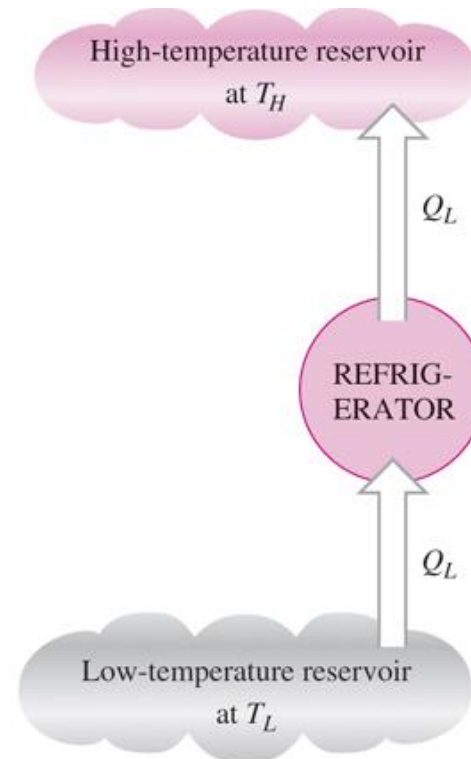


A refrigerator that violates the Clausius statement of the second law.

# Equivalence of the Two Statements



(a) A refrigerator that is powered by a 100 percent efficient heat engine



(b) The equivalent refrigerator

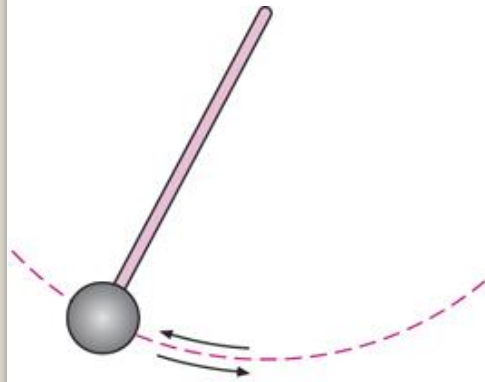
The Kelvin–Planck and the Clausius statements are equivalent in their consequences, and either statement can be used as the expression of the second law of thermodynamics.

Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa.

# REVERSIBLE AND IRREVERSIBLE PROCESSES

**Reversible process:** A process that can be reversed without leaving any trace on the surroundings.

**Irreversible process:** A process that is not reversible.

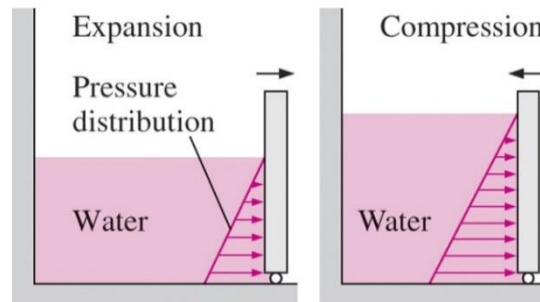


(a) Frictionless pendulum

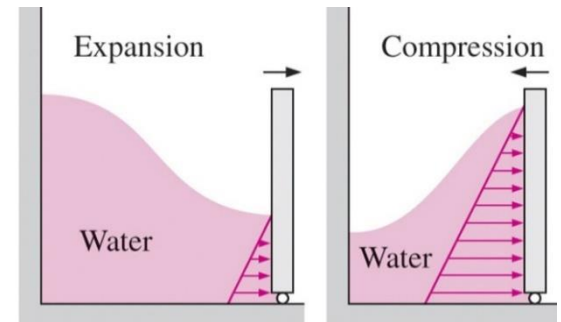
- All the processes occurring in nature are irreversible.
- **Why are we interested in reversible processes?**
- (1) they are easy to analyze and (2) they serve as idealized models (theoretical limits) to which actual processes can be compared.
- Some processes are more irreversible than others.



(b) Quasi-equilibrium expansion and compression of a gas



(a) Slow (reversible) process



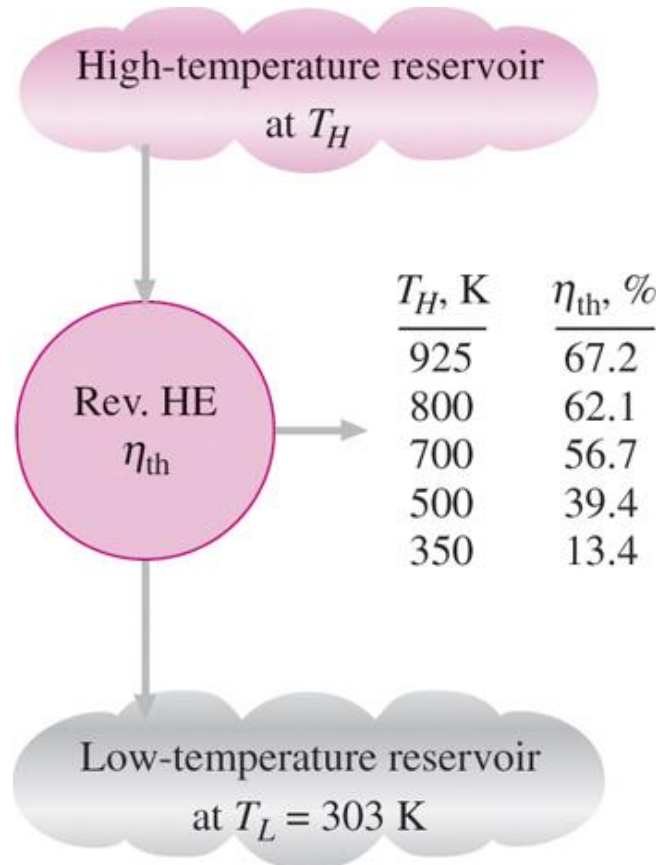
(b) Fast (irreversible) process

Two familiar  
reversible processes.

Reversible processes deliver the most and consume the least work.

# The Quality of Energy

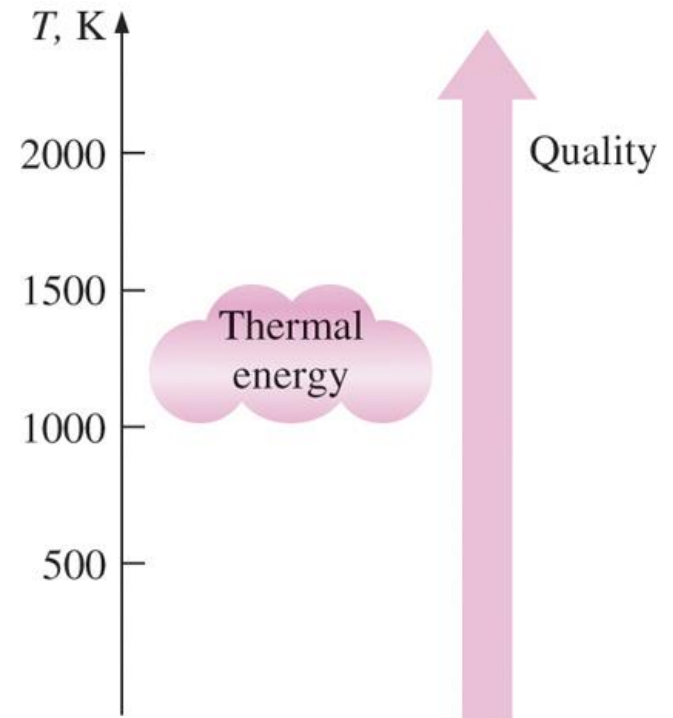
How do you increase the thermal efficiency of a Carnot heat engine? How about for actual heat engines?



The fraction of heat that can be converted to work as a function of source temperature.

$$\eta_{th,rev} = 1 - \frac{T_L}{T_H}$$

**As a system approaches absolute zero, heat becomes harder to extract**



The higher the temperature of the thermal energy, the higher its quality.

# The second law of thermodynamics can be understood through considering these processes:

- A rock will fall if you lift it up and then let go
- Hot pans cool down when taken out from the stove.
- Ice cubes melt in a warm room.

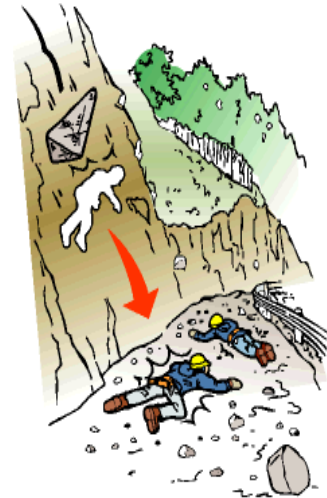


# What's happening in every one of those?

Energy of some kind is changing from being localized (concentrated) somehow to becoming more spread out.

i.e., The potential energy localized in the rock is now totally spread out and dispersed in:

- A little air movement.
- Little heating of air and ground.

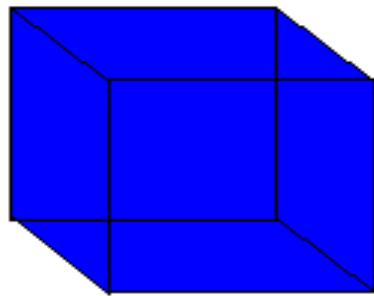


- The second law of thermodynamics states that energy (and matter) tends to become more evenly spread out across the universe.

# What is entropy?

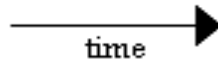
Entropy just measures the **spontaneous dispersal of energy**: or how much energy is spread out in a process as a function of **temperature**.

Entropy



ice cube  
(crystal structure)

minimum entropy  
maximum order



puddle of water  
(no structure)

maximum entropy  
minimum order



# *Entropy*

- *Entropy* a measure of **disorder** in the physical system.
- the movement towards a disordered state is a *spontaneous process*.

So in a simple equation:

$$Entropy = \frac{\text{"Energy dispersed"}}{T}$$

Entropy couldn't be expressed without the inclusion of **absolute temperature**.

- Entropy change  $\Delta S$  shows us exactly how **important** to a system is a **dispersion** of a given amount of energy.

# Entropy

For a reversible engine has the relation between the heat transferred and the reservoir temperatures:

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \quad \Rightarrow \quad \frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H}$$

- ❖ This quantity,  $Q/T$ , is the same for both reservoirs. This conserved quantity is defined as the **change in entropy** ( $\Delta S$ ).

$$\Delta S = \frac{Q}{T} \quad \text{(if the temperature is constant)}$$

Otherwise,

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

# ENTROPY

Unlike energy, entropy is NOT conserved

**Proof:**

A real engine will operate at a lower efficiency than a reversible engine; this means that less heat is converted to work.

$$\eta_{irrev} < \eta_{rev} \Rightarrow 1 - \frac{Q_C}{Q_H} < 1 - \frac{T_C}{T_H} \Rightarrow \frac{Q_C}{Q_H} > \frac{T_C}{T_H} \Rightarrow \frac{Q_C}{T_C} > \frac{Q_H}{T_H}$$

$$\Delta S_{total} = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} > 0$$

Any irreversible process results in an increase of entropy.

# *Entropy*

For a carnot engine

$$\Rightarrow \frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H}$$

Heat supplied  $Q_H$  is positive

Heat rejected  $Q_C$  is negative

$$\Rightarrow \frac{-Q_C}{T_C} = \frac{Q_H}{T_H}$$

$$\Rightarrow \frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0$$

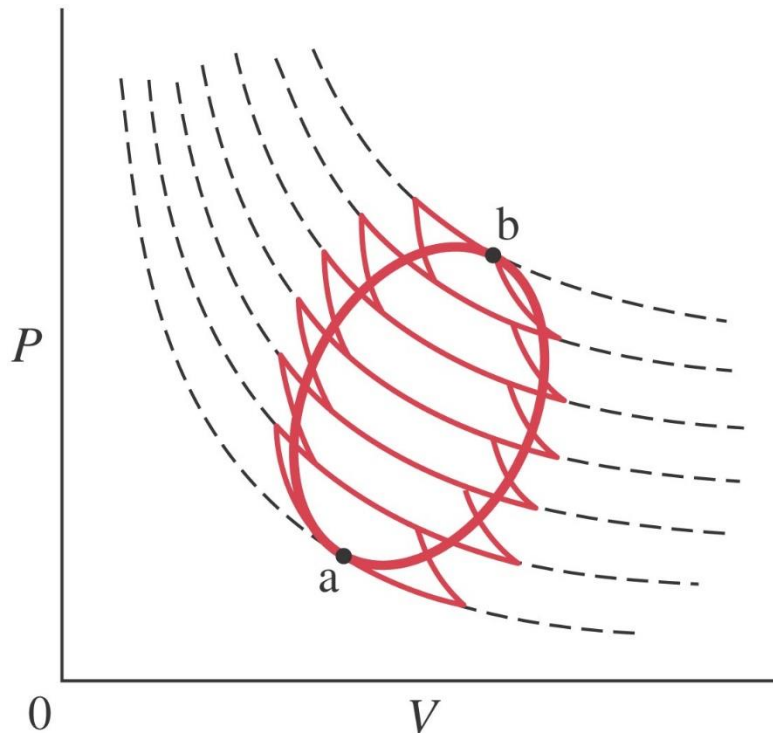
# ENTROPY IN CYCLIC PROCESS

Any cyclic process can be written as a succession of Carnot cycles.

therefore, what is true for a Carnot cycle is true of all reversible cycles.

$$\Rightarrow \frac{dQ_C}{T_C} + \frac{dQ_H}{T_H} = 0$$

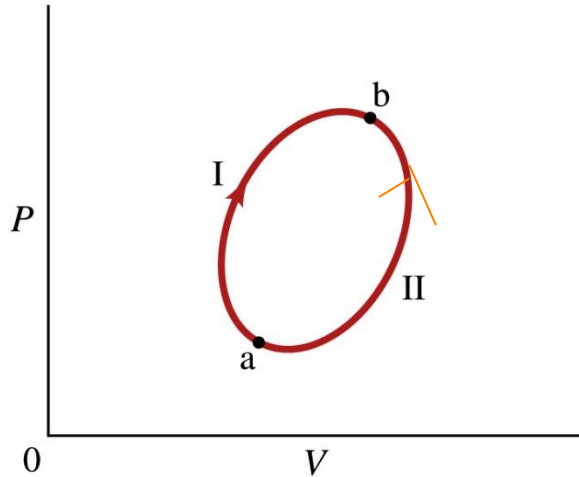
$$\Rightarrow \Delta S_{cycle} = \oint \frac{dQ}{T} = 0$$



This means that entropy is a state variable

# ENTROPY FOR REVERSIBLE PROCESS

*Since entropy is state function*



$$\Rightarrow \Delta S_{total} = \int_{aIb} \frac{dQ}{T}$$

$$\Rightarrow \Delta S_{total} = \int_{aIIb} \frac{dQ}{T}$$

- If a process is adiabatic  $dQ = 0$  &  $\Delta S_{total} = 0$  (Isentropic process)

# MATHEMATICAL STATEMENT OF SECOND LAW

- The total entropy of the universe **increases** whenever an irreversible process occurs.
- The total entropy of the universe is **unchanged** whenever a reversible process occurs.

$$\Delta S_{total} \geq 0$$

*second law of thermodynamics* – the universe, or in any isolated system, the degree of disorder (entropy) can only **increase**.

Is it possible to decrease entropy of a system by any means?

If entropy decreases in a system due to work being done on it, a greater increase in entropy occurs outside the system.

# ENTROPY CHANGES OF AN IDEAL GAS

For one mole or a unit mass of fluid undergoing a mechanically reversible process in a closed system, the first Law

$$dU = dQ_{rev} - dW \quad \Rightarrow dU = dQ_{rev} - PdV$$

## Enthalpy

$$H = U + PV \quad \Rightarrow dH = dU + PdV + VdP$$

Eliminating  $dU$   $\Rightarrow dH = dQ_{rev} - PdV + PdV + VdP$   
 $\Rightarrow dQ_{rev} = dH - VdP$

For an ideal gas,  $dH = C_P dT$  &  $V = \frac{RT}{P}$

$$\Rightarrow \frac{dQ_{rev}}{T} = C_P \frac{dT}{T} - R \frac{dP}{P} \quad \Rightarrow dS = C_P \frac{dT}{T} - R \frac{dP}{P}$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} R \frac{dP}{P}$$

$$\Rightarrow \Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$



# ENTROPY CHANGES OF AN IDEAL GAS

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

For isothermal process,

$$\Rightarrow \Delta S = -R \ln \frac{P_2}{P_1}$$

For ideal gas (at constant temperature):

$$P_1 V_1 = P_2 V_2 \Rightarrow \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

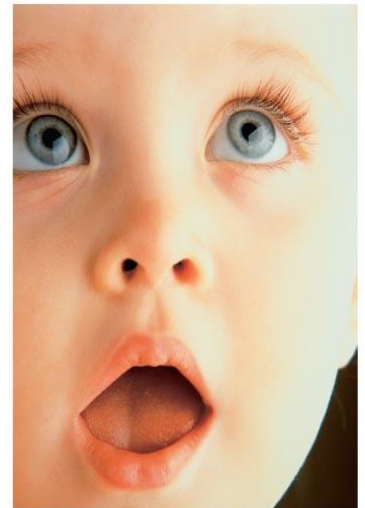
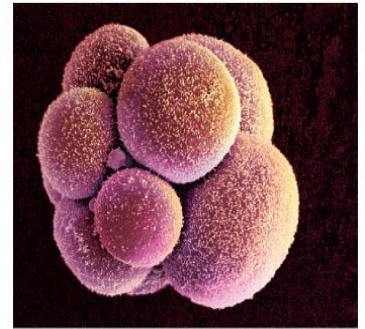
$$\Rightarrow \Delta S = -R \ln \frac{V_1}{V_2}$$

# Life: Randomness to order?

living things are highly ordered, low entropy, structures. Is the second law of thermodynamics violated in the living cells?

**NO!**

- they grow and are sustained because their metabolism generates excess entropy in their surroundings
- Cell is not an isolated system: it takes energy from its environment to generate order within itself.



# The Third Law of Thermodynamics

The absolute entropy is zero for a perfect crystalline substance at absolute zero of temperature (0 K)

$$\lim_{T \rightarrow 0} \Delta S = 0$$

- **Absolute zero is a temperature that an object can get arbitrarily close to, but never attain.**
- **Temperatures as low as  $2.0 \times 10^{-8}$  K have been achieved in the laboratory, but absolute zero will remain ever elusive – there is simply nowhere to “put” that last little bit of energy.**

# The Third Law of Thermodynamics

**It is impossible to lower the temperature of an object to absolute zero in a finite number of steps.**

- **No system can reach absolute zero**
- **This is one reason we use the Kelvin temperature scale. ( you never have to worry about dividing by zero in an equation!)**

# Practical uses: surroundings & system

## Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

- At constant pressure,  $q_{sys}$  is simply  $\Delta H$  for the system.

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H}{T}$$

# Link S and $\Delta H$ : Phase changes

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H}{T}$$

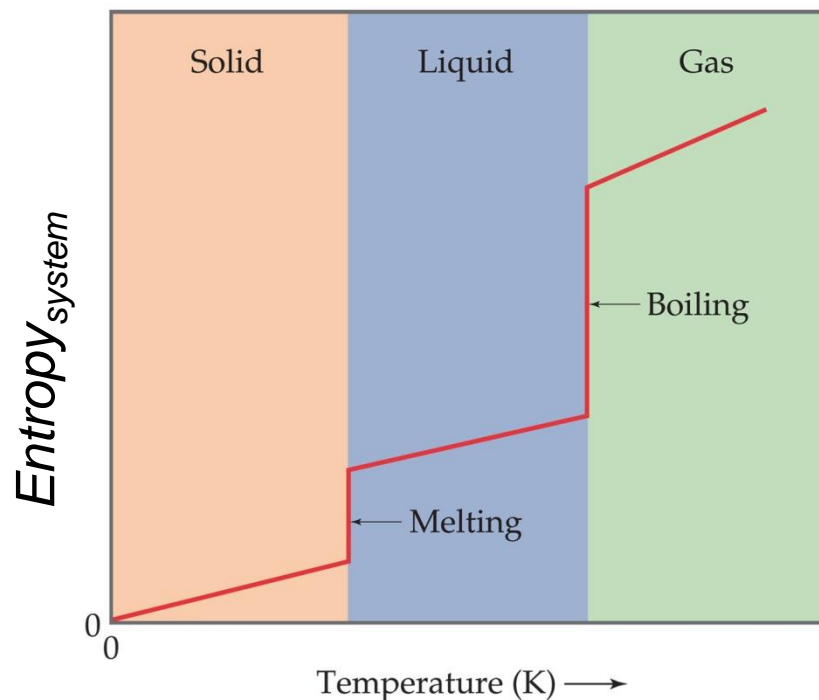
A phase change is isothermal (no change in T).

For water:

$$\Delta H_{\text{fusion}} = 6 \text{ kJ/mol}$$

$$\Delta H_{\text{vap}} = 41 \text{ kJ/mol}$$

If we do this reversibly:  $\Delta S_{surr} = -\Delta S_{sys}$



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# Calculation of Absolute entropy

- In comparison with internal energy and enthalpy, which are calculated relative to an arbitrary reference state, **entropy is a reference property and is absolute, as are pressure, volume, and temperature.**
- Third law of thermodynamics can be utilized to calculate the absolute entropy of substances at a given temperature by assigning the value zero for entropy of the crystalline form of the substance at absolute zero.

$$S = \int_0^{T_f} \frac{C_{P,S} dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{C_{P,L} dT}{T} + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{C_{P,G} dT}{T}$$

Where,

- $C_{P,S}$ ,  $C_{P,L}$  and  $C_{P,G}$  are specific heat of solid, liquid and gas respectively.
- $\Delta H_f$  and  $\Delta H_v$  are the latent heats of fusion and vaporization respectively

# Entropy vs. Enthalpy

The enthalpy of a system is defined as:

$$H = U + PV$$

And the change in enthalpy =

$$\Delta H = \Delta U + \Delta (PV)$$

For constant pressure processes:

$$\Delta H = \Delta U + P\Delta V = \Delta U + \text{Work} = Q!$$

- Enthalpy is sometimes described as the *heat content* of a system under a **given pressure**
- Adding or removing energy through heat is the *only* way to change the enthalpy.

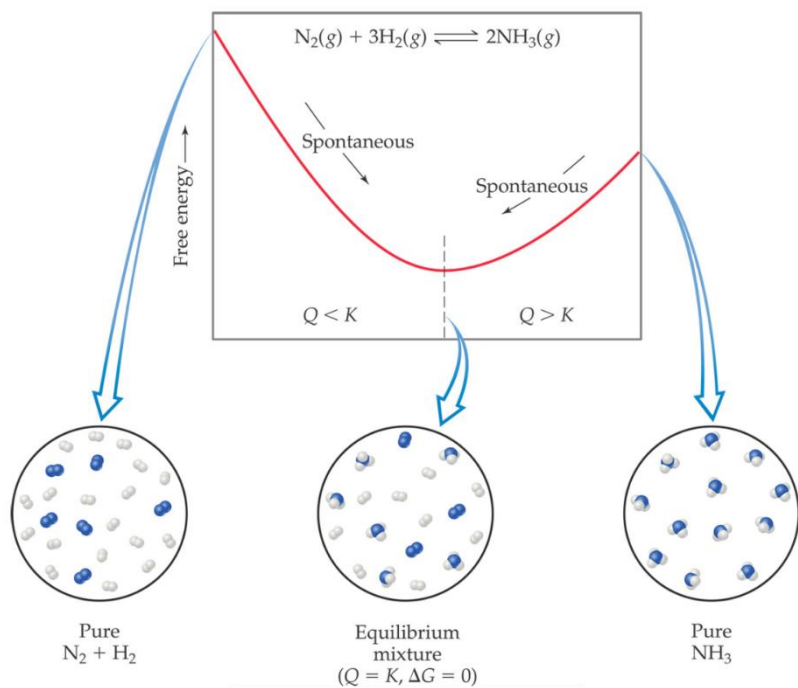


# Entropy vs. Enthalpy

**ENTHALPHY:** Is the energy content of a process (chemical, thermodynamic, mechanical, etc) that can be recovered. **It is also described as useful energy.**

**ENTROPY:** Is the energy content of a process (chemical, thermodynamic, mechanical, etc) that **CANNOT** be recovered. **It is also described as chaos.**

# Gibbs Free Energy – Chemical reaction



1. If  $\Delta G$  is negative, the forward reaction is spontaneous.
2. If  $\Delta G$  is 0, the system is at equilibrium.
3. If  $\Delta G$  is positive, the reaction is spontaneous in the reverse direction.

# Free Energy and Temperature

- The temperature dependence of free energy comes from the entropy term.

TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	-	Spontaneous at all temperatures	$2 \text{ O}_3(\text{g}) \longrightarrow 3 \text{ O}_2(\text{g})$
+	-	+	+	Nonspontaneous at all temperatures	$3 \text{ O}_2(\text{g}) \longrightarrow 2 \text{ O}_3(\text{g})$
-	-	+	+ or -	Spontaneous at low $T$ ; nonspontaneous at high $T$	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$
+	+	-	+ or -	Spontaneous at high $T$ ; nonspontaneous at low $T$	$\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$

By knowing the sign (+ or -) of  $\Delta S$  and  $\Delta H$ , we can get the sign of  $\Delta G$  and determine if a reaction is spontaneous.