

# *Chapter 15*

## ***Thermodynamics***

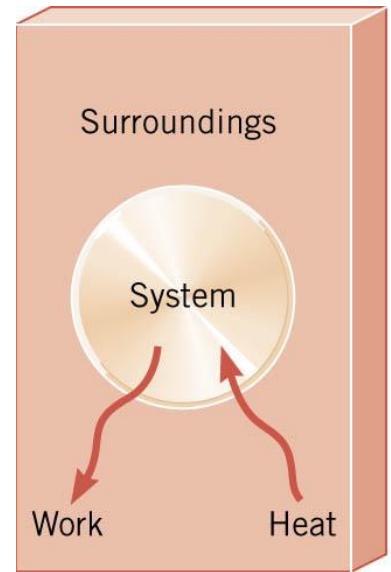
## 15.1 Thermodynamic Systems and Their Surroundings

**Thermodynamics** is the branch of physics that is built upon the fundamental laws that heat and work obey.

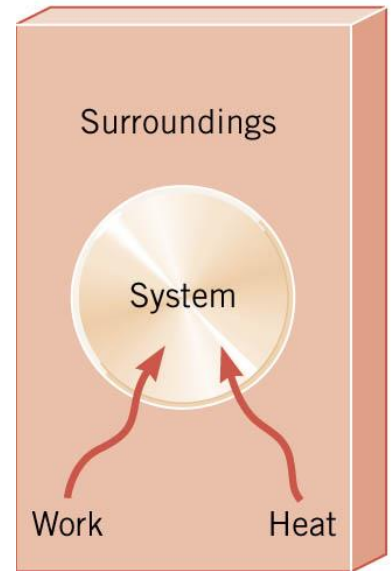
The collection of objects on which attention is being focused is called the **system**, while everything else in the environment is called the **surroundings**.

Walls that permit heat flow are called **diathermal walls**, while walls that do not permit heat flow are called **adiabatic walls**.

To understand thermodynamics, it is necessary to describe the **state of a system**.



(a)

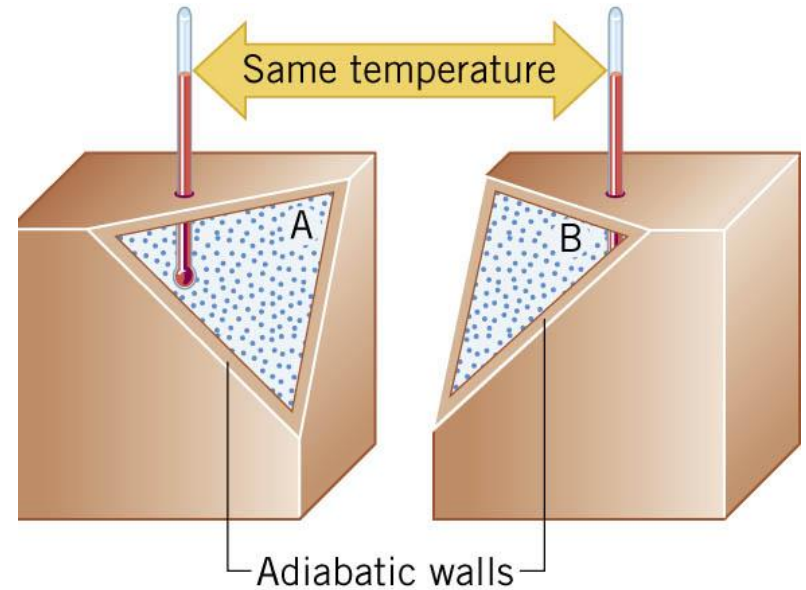


(b)

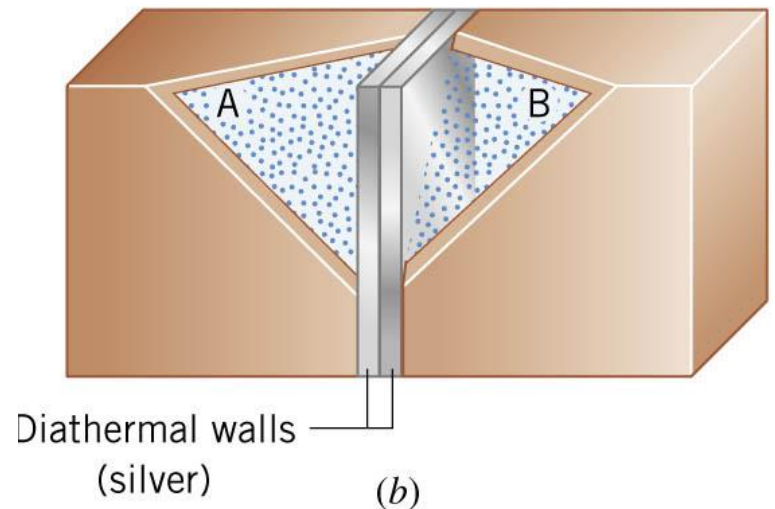
## 15.2 The Zeroth Law of Thermodynamics

Two systems are said to be in **thermal equilibrium** if there is no heat flow between them when they are brought into contact.

Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.



(a)

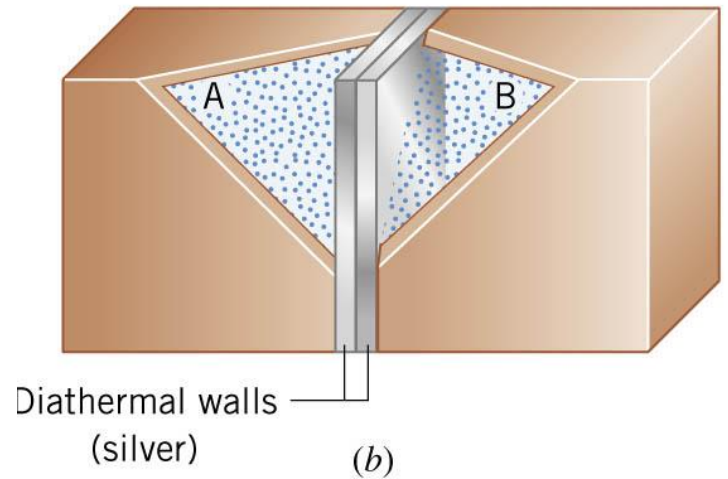
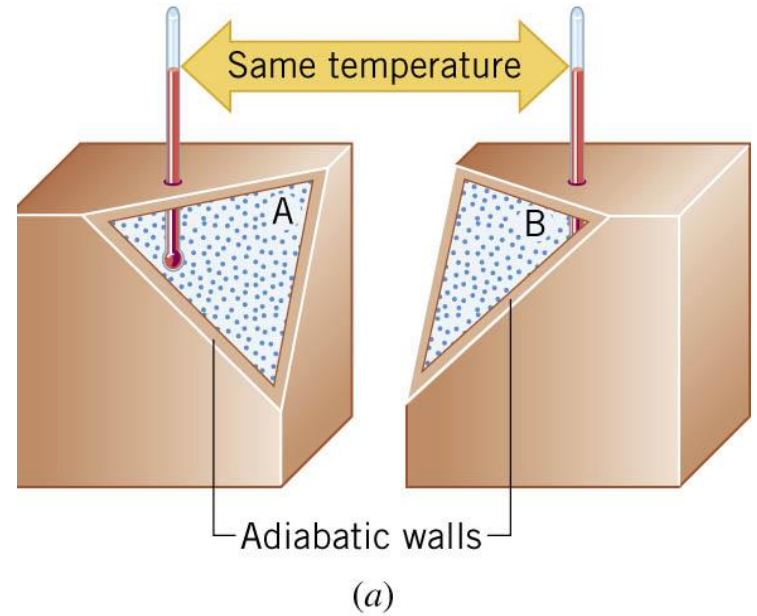


(b)

## 15.2 The Zeroth Law of Thermodynamics

### THE ZEROth LAW OF THERMODYNAMICS

Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.



## 15.3 *The First Law of Thermodynamics*

Suppose that a system gains heat  $Q$  and that is the only effect occurring.

Consistent with the law of conservation of energy, the internal energy of the system changes:

$$\Delta U = U_f - U_i = Q$$

Heat is positive when the system gains heat and negative when the system loses heat.

## 15.3 *The First Law of Thermodynamics*

If a system does work  $W$  on its surroundings and there is no heat flow, conservation of energy indicates that the internal energy of the system will decrease:

$$\Delta U = U_f - U_i = -W$$

Work is positive when it is done by the system and negative when it is done on the system.

## 15.3 *The First Law of Thermodynamics*

### THE FIRST LAW OF THERMODYNAMICS

The internal energy of a system changes due to heat and work:

$$\Delta U = U_f - U_i = Q - W$$

Heat is positive when the system gains heat and negative when the system loses heat.

Work is positive when it is done by the system and negative when it is done on the system.

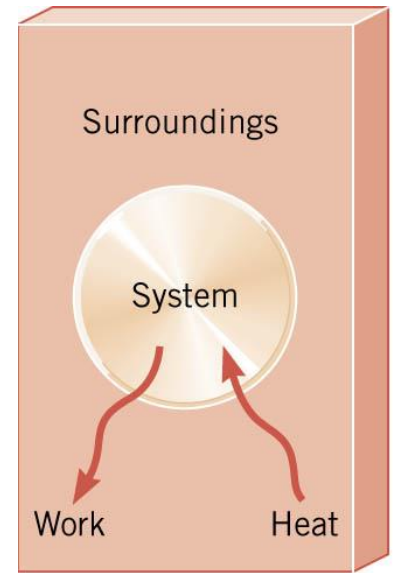
## 15.3 The First Law of Thermodynamics

### Example 1 Positive and Negative Work

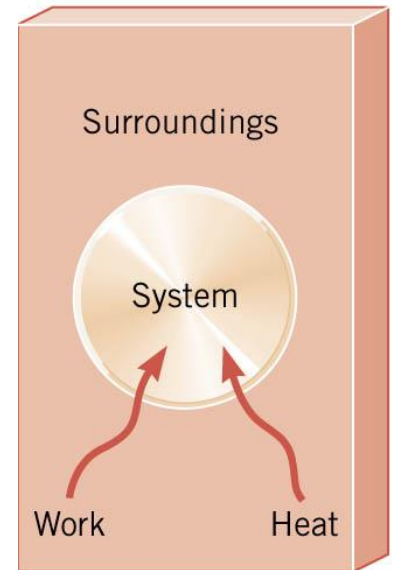
In part *a* of figure, the system gains 1500J of heat and 2200J of work is done by the system on its surroundings.

In part *b*, the system also gains 1500J of heat, but 2200J of work is done on the system.

In each case, determine the change in internal energy of the system.



(a)



(b)

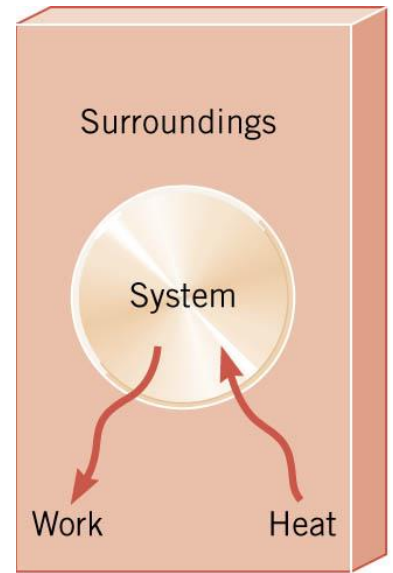


## 15.3 The First Law of Thermodynamics

(a)

$$\Delta U = Q - W$$

$$= (+1500 \text{ J}) - (+2200 \text{ J}) = -700 \text{ J}$$

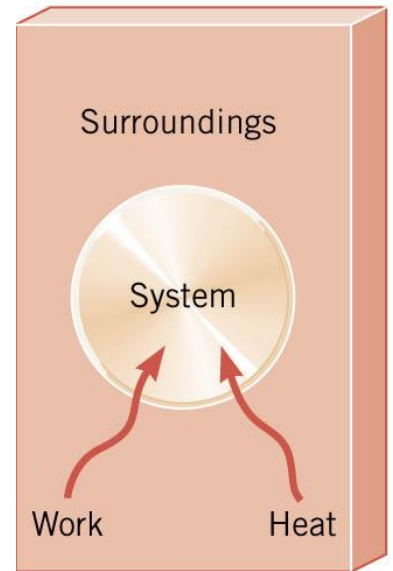


(a)

(b)

$$\Delta U = Q - W$$

$$= (+1500 \text{ J}) - (-2200 \text{ J}) = +3700 \text{ J}$$



(b)

## 15.3 *The First Law of Thermodynamics*

### ***Example 2 An Ideal Gas***

The temperature of three moles of a monatomic ideal gas is reduced from 540K to 350K as 5500J of heat flows into the gas.

Find (a) the change in internal energy and (b) the work done by the gas.

$$\Delta U = U_f - U_i = Q - W$$

$$U = \frac{3}{2} nRT$$

### 15.3 The First Law of Thermodynamics

$$\begin{aligned} \text{(a)} \quad \Delta U &= \frac{3}{2} nRT_f - \frac{3}{2} nRT_i \\ &= \frac{3}{2} (3.0 \text{ mol})(8.31 \text{ J}/(\text{mol} \cdot \text{K}))(350 \text{ K} - 540 \text{ K}) = -7100 \text{ J} \end{aligned}$$

$$\text{(b)} \quad W = Q - \Delta U = 5500 \text{ J} - (-7100 \text{ J}) = 12600 \text{ J}$$

## 15.4 Thermal Processes

A ***quasi-static*** process is one that occurs slowly enough that a uniform temperature and pressure exist throughout all regions of the system at all times.

***isobaric***: constant pressure

***isochoric***: constant volume

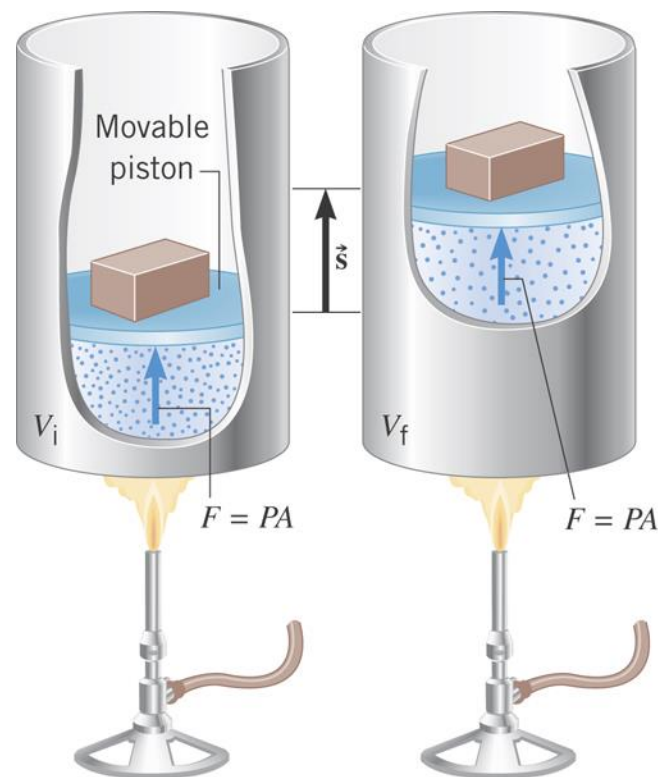
***isothermal***: constant temperature

***adiabatic***: no transfer of heat

## 15.4 Thermal Processes

An **isobaric** process is one that occurs at constant pressure.

$$W = Fs = P(As) = P\Delta V$$



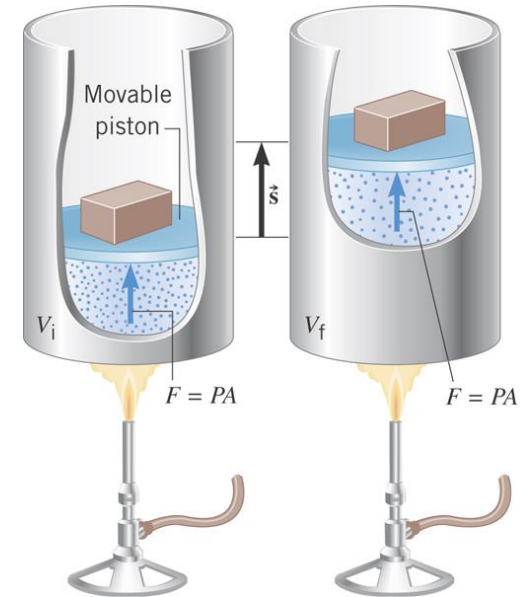
**Isobaric process:** 
$$W = P\Delta V = P(V_f - V_i)$$

## 15.4 Thermal Processes

### Example 3 Isobaric Expansion of Water

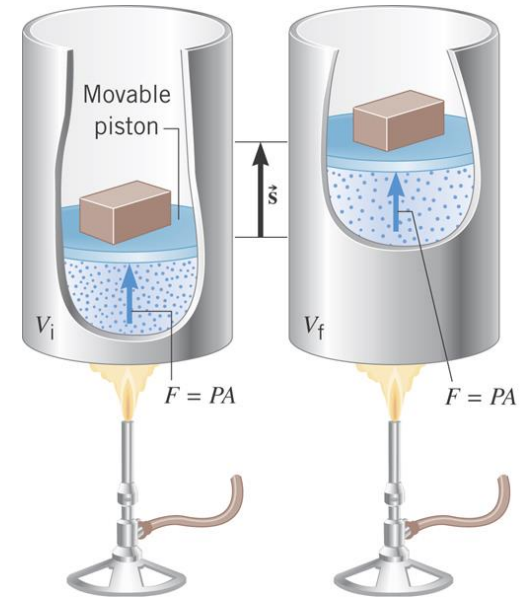
One gram of water is placed in the cylinder and the pressure is maintained at  $2.0 \times 10^5 \text{ Pa}$ . The temperature of the water is raised by  $31^\circ \text{C}$ . The water is in the liquid phase and expands by the small amount of  $1.0 \times 10^{-8} \text{ m}^3$ .

Find the work done and the change in internal energy.



## 15.4 Thermal Processes

$$W = P\Delta V$$
$$= (2.0 \times 10^5 \text{ Pa})(1.0 \times 10^{-8} \text{ m}^3) = 0.0020 \text{ J}$$

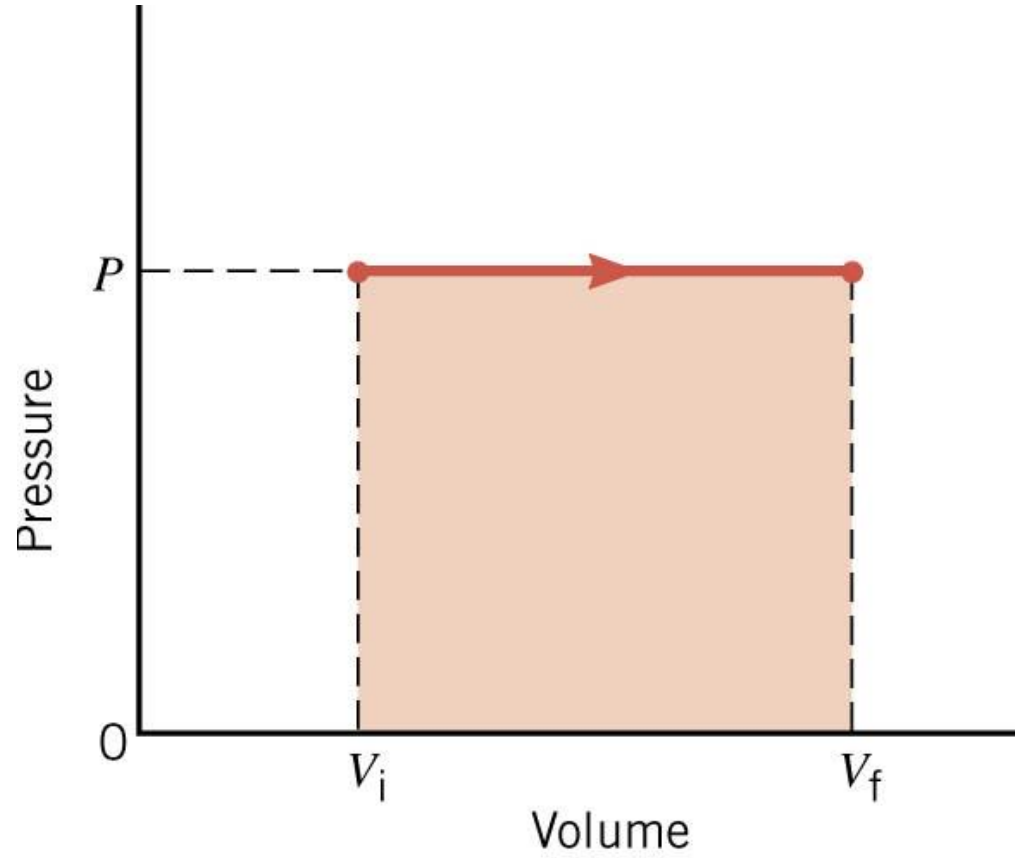


$$\Delta U = Q - W = 130 \text{ J} - 0.0020 \text{ J} = 130 \text{ J}$$

$$Q = mc\Delta T = (0.0010 \text{ kg})[4186 \text{ J}/(\text{kg} \cdot \text{C}^\circ)](31 \text{ C}^\circ) = 130 \text{ J}$$

15.4 Thermal Processes

$$W = P\Delta V = P(V_f - V_i)$$





# 15.4 Thermal Processes

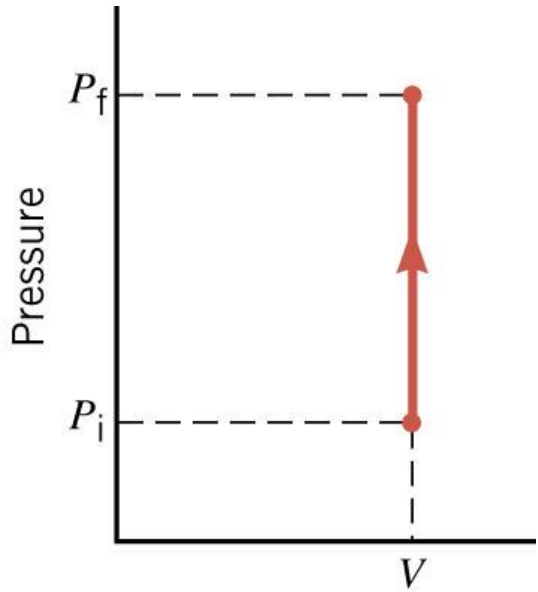
**isochoric:** constant volume

$$\Delta U = Q - W = Q$$

$$W = 0$$



(a)



Volume

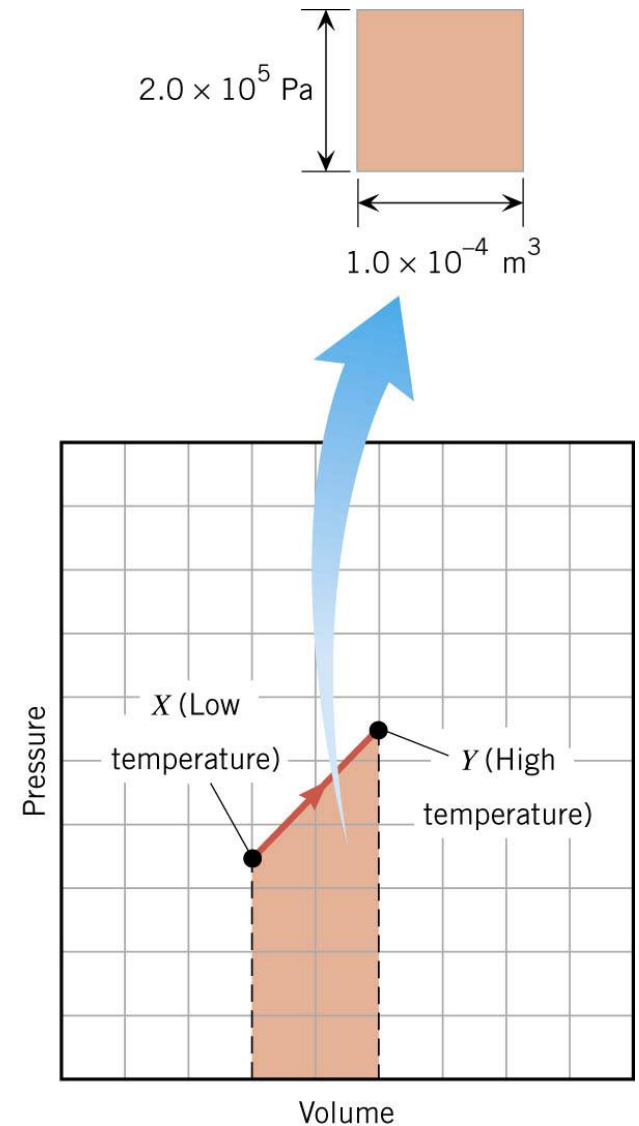
(b)

## 15.4 Thermal Processes

### Example 4 Work and the Area Under a Pressure-Volume Graph

Determine the work for the process in which the pressure, volume, and temperature of a gas are changed along the straight line in the figure.

*The area under a pressure-volume graph is the work for any kind of process.*

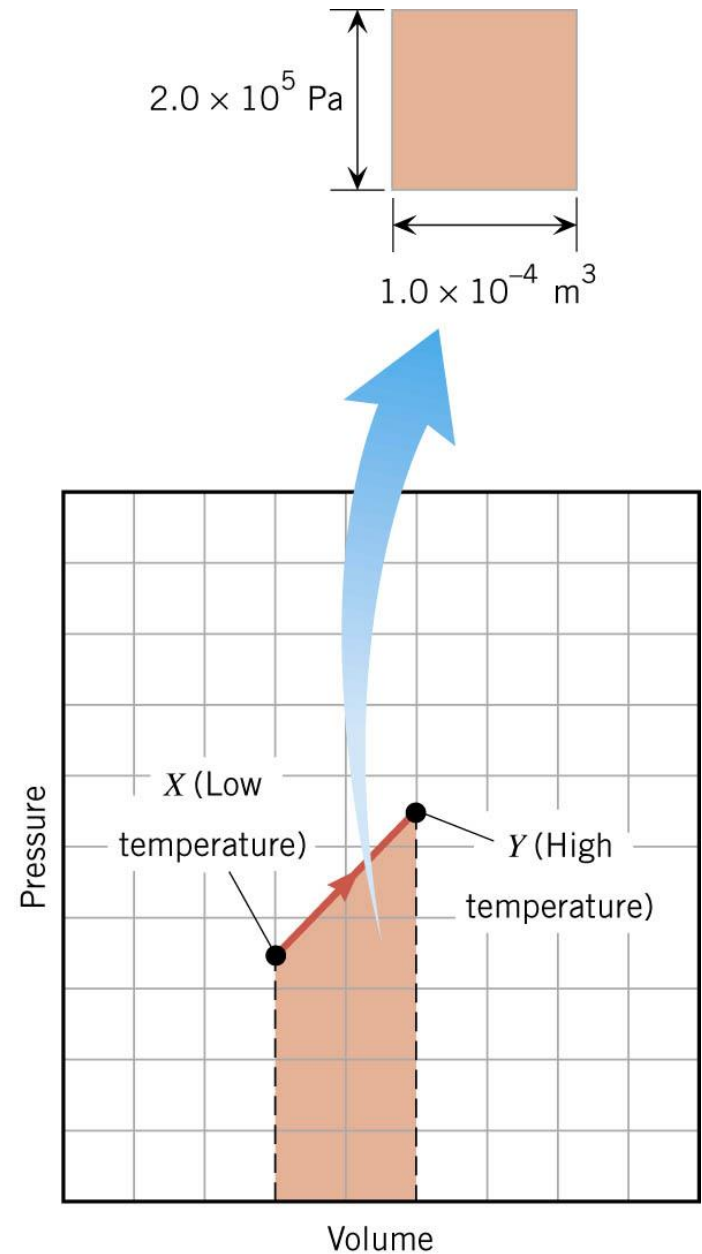


## 15.4 Thermal Processes

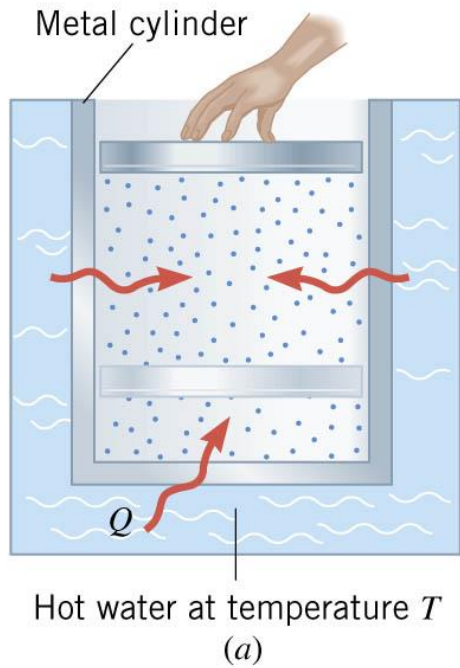
Since the volume increases, the work is positive.

Estimate that there are 8.9 colored squares in the drawing.

$$W = 8.9(2.0 \times 10^5 \text{ Pa})(1.0 \times 10^{-4} \text{ m}^3) \\ = +180 \text{ J}$$



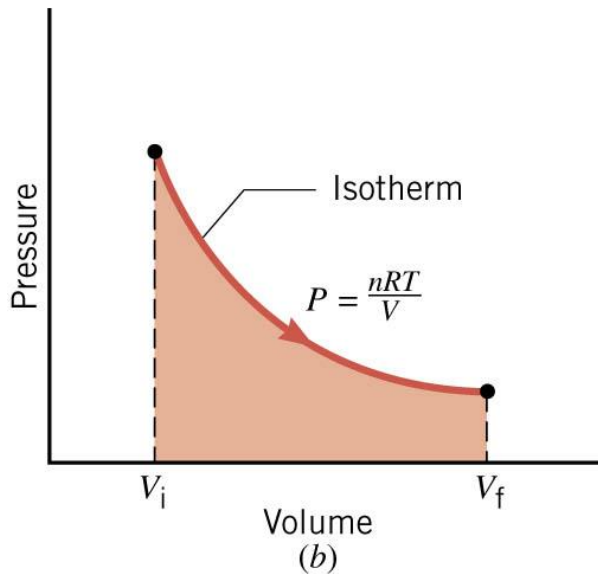
## 15.5 Thermal Processes Using an Ideal Gas



### ISOTHERMAL EXPANSION OR COMPRESSION

*Isothermal expansion or compression of an ideal gas*

$$W = nRT \ln \left( \frac{V_f}{V_i} \right)$$



### **Example 5 Isothermal Expansion of an Ideal Gas**

Two moles of the monatomic gas argon expand isothermally at 298K from an initial volume of  $0.025\text{m}^3$  to a final volume of  $0.050\text{m}^3$ . Assuming that argon is an ideal gas, find (a) the work done by the gas, (b) the change in internal energy of the gas, and (c) the heat supplied to the gas.

## 15.5 Thermal Processes Using and Ideal Gas

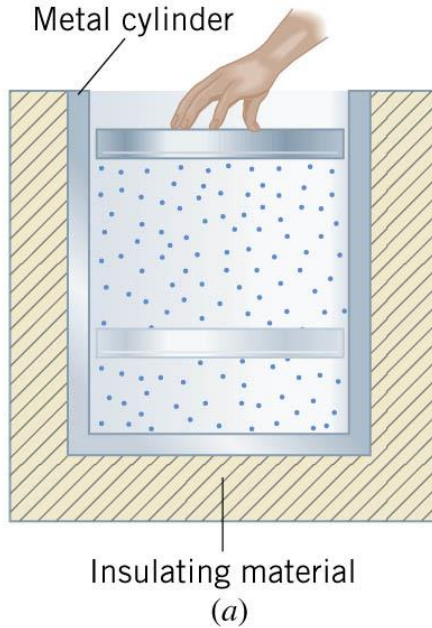
$$\begin{aligned} \text{(a)} \quad W &= nRT \ln\left(\frac{V_f}{V_i}\right) \\ &= (2.0 \text{ mol})(8.31 \text{ J}/(\text{mol} \cdot \text{K}))(298 \text{ K}) \ln\left(\frac{0.050 \text{ m}^3}{0.025 \text{ m}^3}\right) = +3400 \text{ J} \end{aligned}$$

$$\text{(b)} \quad \Delta U = \frac{3}{2} nRT_f - \frac{3}{2} nRT_i = 0$$

$$\text{(c)} \quad \Delta U = Q - W$$

$$Q = W = +3400 \text{ J}$$

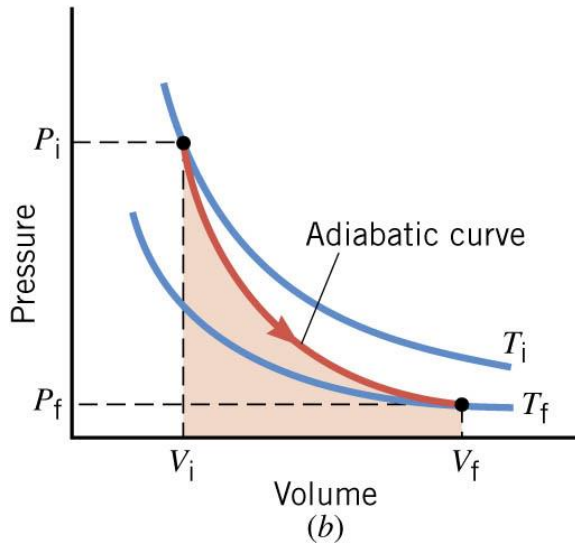
## 15.5 Thermal Processes Using and Ideal Gas



### ADIABATIC EXPANSION OR COMPRESSION

**Adiabatic expansion or compression of a monatomic ideal gas**

$$W = \frac{3}{2} nR(T_i - T_f)$$



**Adiabatic expansion or compression of a monatomic ideal gas**

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\gamma = c_P / c_V$$

## 15.6 Specific Heat Capacities

To relate heat and temperature change in solids and liquids, we used:

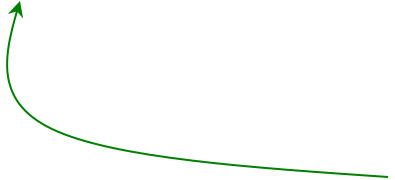
$$Q = mc\Delta T$$



specific heat  
capacity

The amount of a gas is conveniently expressed in moles, so we write the following analogous expression:

$$Q = Cn\Delta T$$



molar specific  
heat capacity



## 15.6 Specific Heat Capacities

For gases it is necessary to distinguish between the molar specific heat capacities which apply to the conditions of constant pressure and constant volume:

$$C_V, C_P$$

$$U = \frac{3}{2}nRT$$

$$\underbrace{Q_{\text{constant pressure}} = \Delta U + W}_{\text{first law of thermodynamics}} = \overbrace{\frac{3}{2}nR(T_f - T_i)} + \underbrace{nR(T_f - T_i)}_{W = P\Delta V} = \frac{5}{2}nR\Delta T$$

first law of  
thermodynamics

$$W = P\Delta V$$

**constant pressure  
for a monatomic  
ideal gas**

$$C_P = \frac{5}{2}R$$

## 15.6 Specific Heat Capacities

$$U = \frac{3}{2}nRT$$

$$\underbrace{Q_{\text{constant volume}} = \Delta U + W}_{\text{first law of thermodynamics}} = \overbrace{\frac{3}{2}nR(T_f - T_i)} + 0 = \frac{3}{2}nR\Delta T$$

first law of  
thermodynamics

**constant pressure  
for a monatomic  
ideal gas**

$$C_V = \frac{3}{2}R$$

**monatomic  
ideal gas**

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

**any ideal gas**

$$C_P - C_V = R$$

## 15.7 *The Second Law of Thermodynamics*

The second law is a statement about the natural tendency of heat to flow from hot to cold, whereas the first law deals with energy conservation and focuses on both heat and work.

### THE SECOND LAW OF THERMODYNAMICS: THE HEAT FLOW STATEMENT

Heat flows spontaneously from a substance at a higher temperature to a substance at a lower temperature and does not flow spontaneously in the reverse direction.

## 15.8 Heat Engines

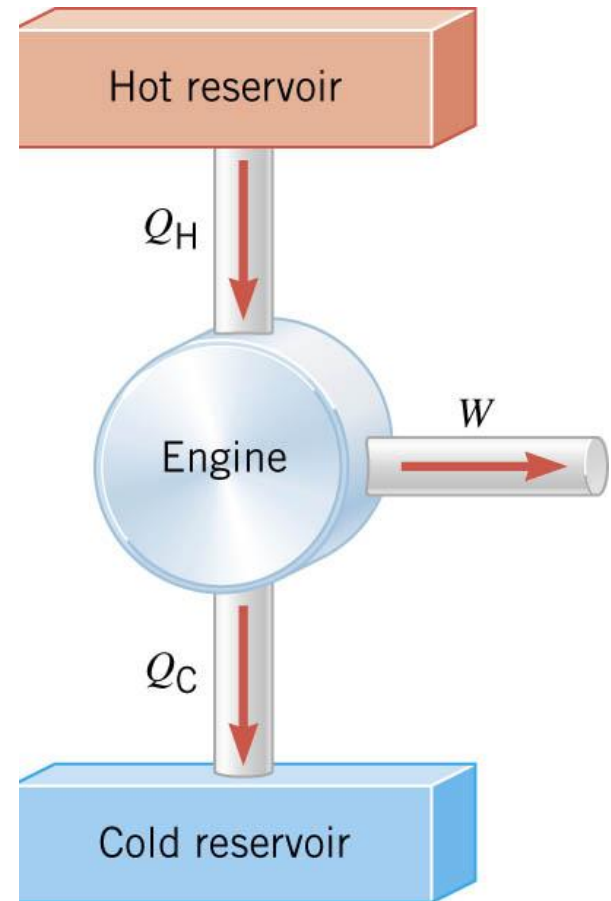
A **heat engine** is any device that uses heat to perform work. It has three essential features.

1. Heat is supplied to the engine at a relatively high temperature from a place called the *hot reservoir*.
2. Part of the input heat is used to perform work by the *working substance* of the engine.
3. The remainder of the input heat is rejected to a place called the *cold reservoir*.

$|Q_H|$  = magnitude of input heat

$|Q_C|$  = magnitude of rejected heat

$|W|$  = magnitude of the work done



## 15.8 Heat Engines

The **efficiency** of a heat engine is defined as the ratio of the work done to the input heat:

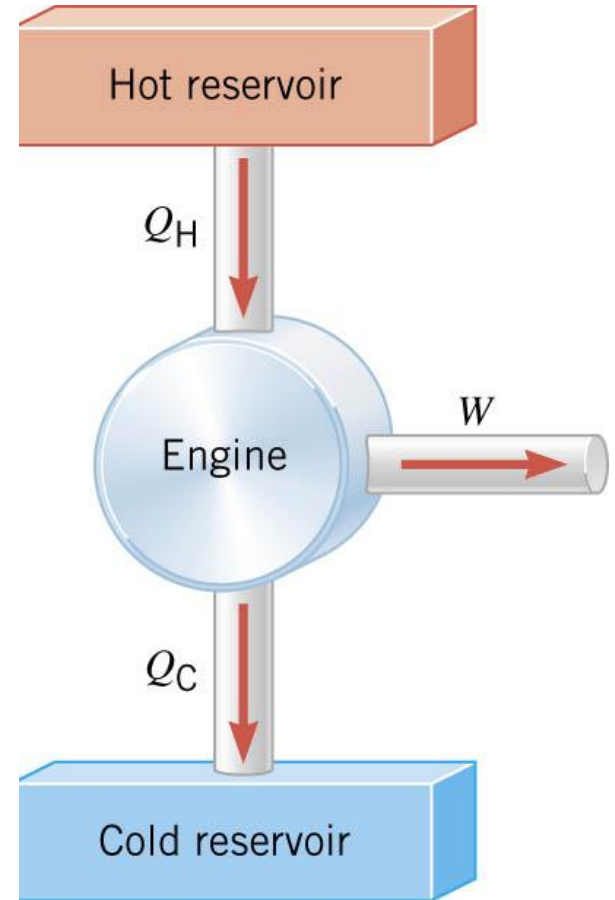
$$e = \frac{|W|}{|Q_H|}$$

If there are no other losses, then

$$|Q_H| = |W| + |Q_C|$$



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



## 15.8 Heat Engines

### Example 6 An Automobile Engine

An automobile engine has an efficiency of 22.0% and produces 2510 J of work. How much heat is rejected by the engine?

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

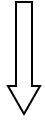
$$|Q_H| = |W| + |Q_C|$$



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

## 15.8 Heat Engines

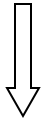
$$|Q_H| = |W| + |Q_C|$$



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



$$|Q_C| = |Q_H| - |W|$$



$$|Q_C| = \frac{|W|}{e} - |W| = |W| \left( \frac{1}{e} - 1 \right)$$

$$= (2510 \text{ J}) \left( \frac{1}{0.220} - 1 \right) = 8.90 \times 10^3 \text{ J}$$

## 15.9 Carnot's Principle and the Carnot Engine

*A reversible process is one in which both the system and the environment can be returned to exactly the states they were in before the process occurred.*

### CARNOT'S PRINCIPLE: AN ALTERNATIVE STATEMENT OF THE SECOND LAW OF THERMODYNAMICS

No irreversible engine operating between two reservoirs at constant temperatures can have a greater efficiency than a reversible engine operating between the same temperatures. Furthermore, all reversible engines operating between the same temperatures have the same efficiency.



## 15.9 Carnot's Principle and the Carnot Engine

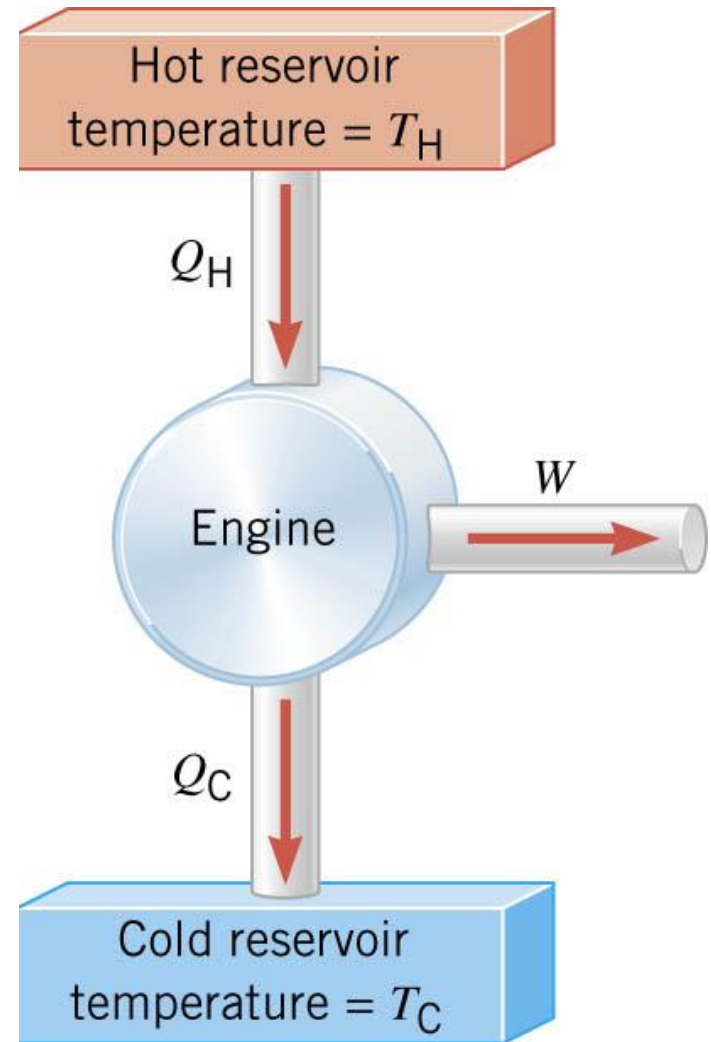
The **Carnot engine** is useful as an idealized model.

All of the heat input originates from a single temperature, and all the rejected heat goes into a cold reservoir at a single temperature.

Since the efficiency can only depend on the reservoir temperatures, the ratio of heats can only depend on those temperatures.

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

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



## 15.9 Carnot's Principle and the Carnot Engine

### **Example 7 A Tropical Ocean as a Heat Engine**

Water near the surface of a tropical ocean has a temperature of 298.2 K, whereas the water 700 meters beneath the surface has a temperature of 280.2 K. It has been proposed that the warm water be used as the hot reservoir and the cool water as the cold reservoir of a heat engine. Find the maximum possible efficiency for such an engine.

$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H}$$

## 15.9 Carnot's Principle and the Carnot Engine

$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{280.2 \text{ K}}{298.2 \text{ K}} = 0.06036$$

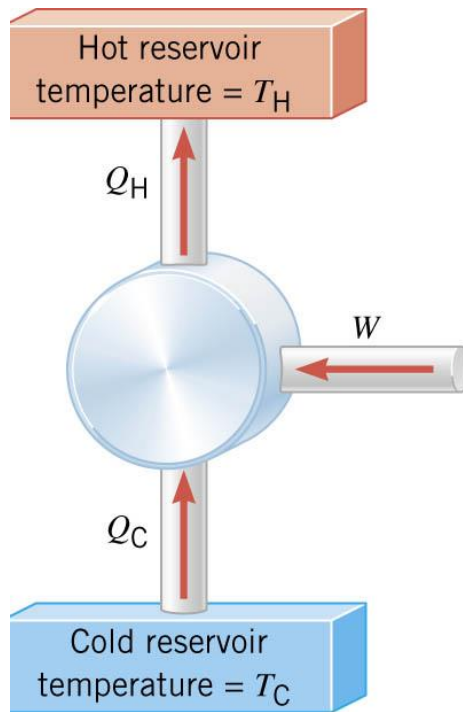
## 15.9 Carnot's Principle and the Carnot Engine

### ***Conceptual Example 8*** Natural Limits on the Efficiency of a Heat Engine

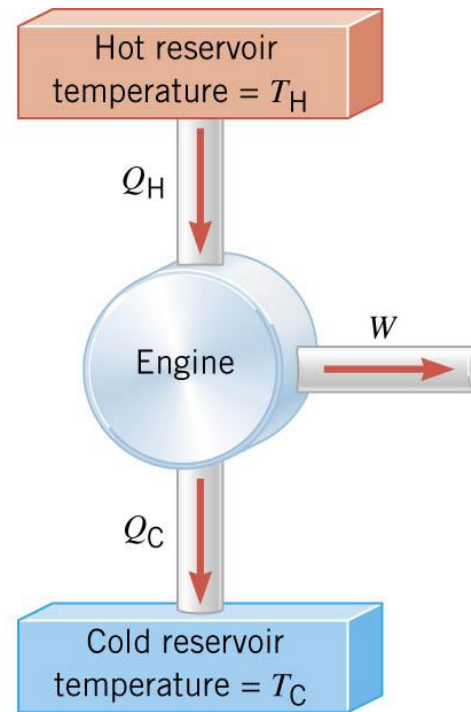
Consider a hypothetical engine that receives 1000 J of heat as input from a hot reservoir and delivers 1000J of work, rejecting no heat to a cold reservoir whose temperature is above 0 K. Decide whether this engine violates the first or second law of thermodynamics.

## 15.10 Refrigerators, Air Conditioners, and Heat Pumps

Refrigerators, air conditioners, and heat pumps are devices that make heat flow from cold to hot. This is called the **refrigeration process**.

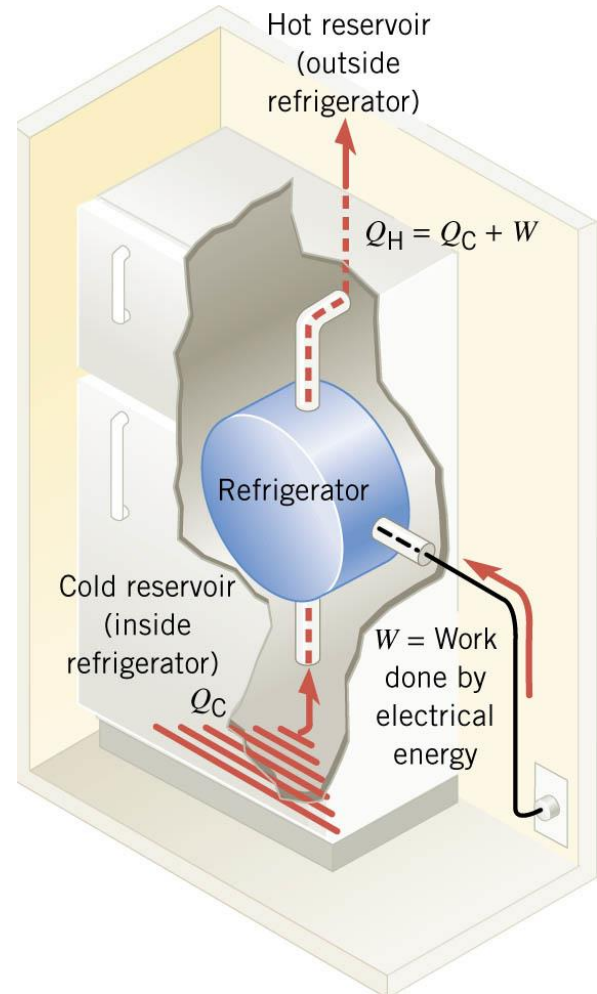
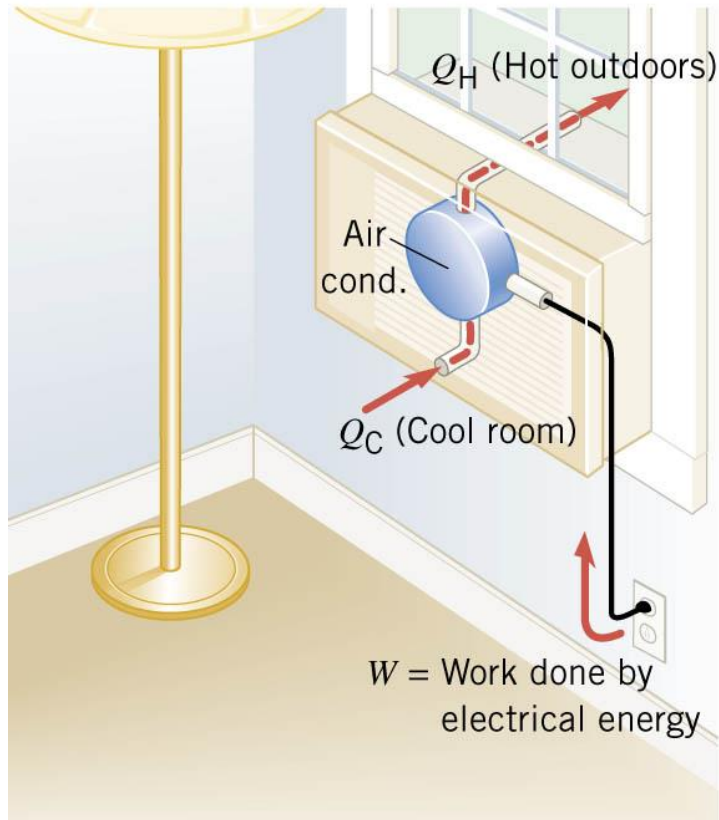


Refrigeration Process



Engine Process

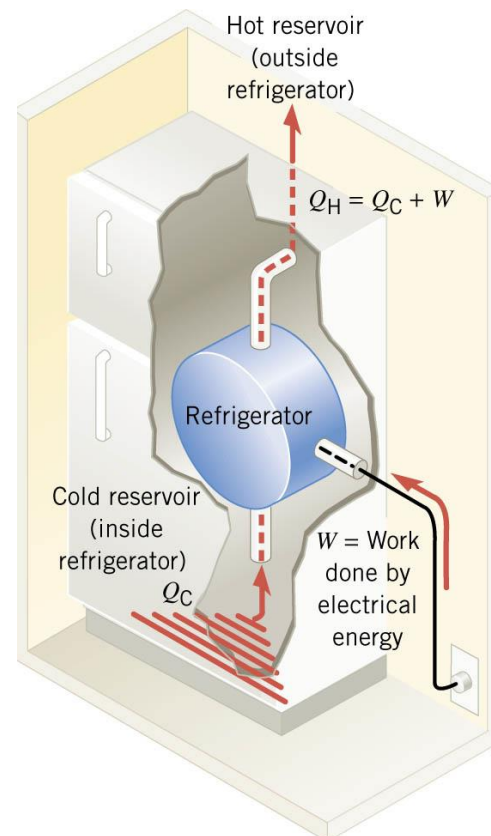
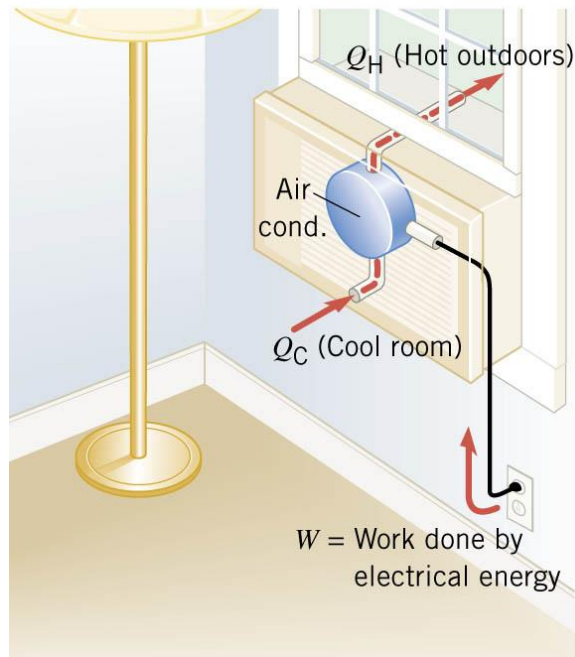
## 15.10 Refrigerators, Air Conditioners, and Heat Pumps



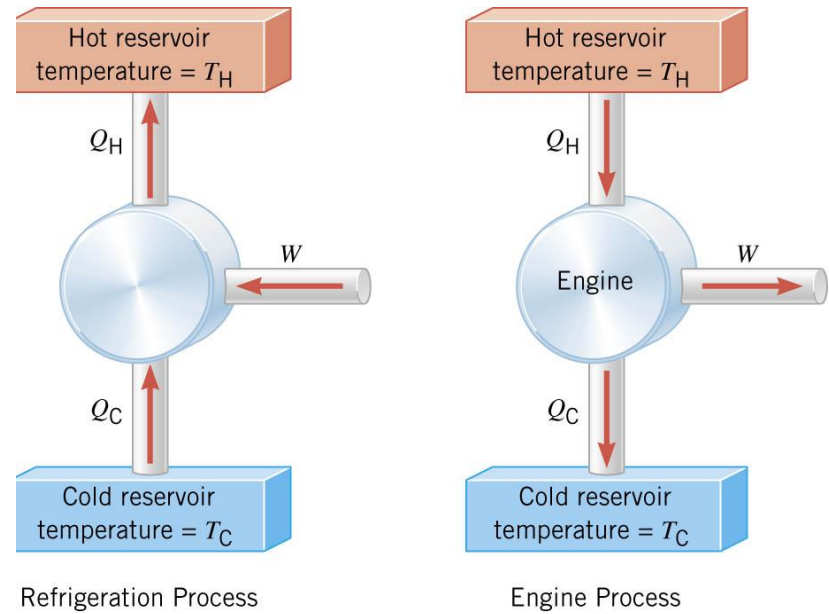
## 15.10 Refrigerators, Air Conditioners, and Heat Pumps

### Conceptual Example 9 You Can't Beat the Second Law of Thermodynamics

Is it possible to cool your kitchen by leaving the refrigerator door open or to cool your room by putting a window air conditioner on the floor by the bed?



## 15.10 Refrigerators, Air Conditioners, and Heat Pumps



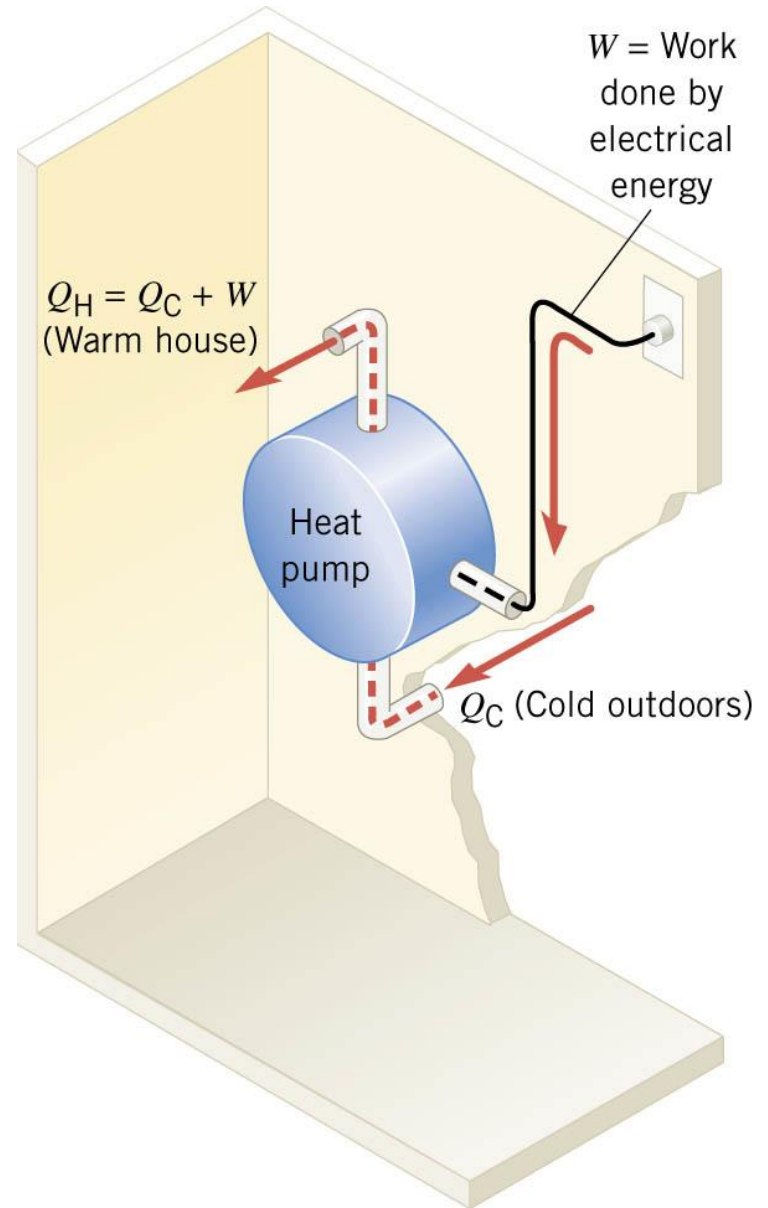
***Refrigerator or  
air conditioner***

$$\text{Coefficient of performance} = \frac{|Q_C|}{|W|}$$



## 15.10 Refrigerators, Air Conditioners, and Heat Pumps

The **heat pump** uses work to make heat from the wintry outdoors flow into the house.




## 15.10 Refrigerators, Air Conditioners, and Heat Pumps

### Example 10 A Heat Pump

An ideal, or Carnot, heat pump is used to heat a house at 294 K. How much work must the pump do to deliver 3350 J of heat into the house on a day when the outdoor temperature is 273 K?

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


$$|W| = |Q_H| - |Q_C|$$


$$|W| = |Q_H| \left( 1 - \frac{T_C}{T_H} \right)$$

## 15.10 Refrigerators, Air Conditioners, and Heat Pumps

$$|W| = |Q_H| \left( 1 - \frac{T_C}{T_H} \right) = (3350 \text{ J}) \left( 1 - \frac{273 \text{ K}}{294 \text{ K}} \right) = 239 \text{ J}$$

*heat  
pump*

$$\text{Coefficient of performance} = \frac{|Q_H|}{|W|}$$

## 15.11 Entropy

In general, irreversible processes cause us to lose some, but not necessarily all, of the ability to do work. This partial loss can be expressed in terms of a concept called **entropy**.

**Carnot engine**

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

**entropy change**

$$\Delta S = \left( \frac{Q}{T} \right)_R$$

reversible

## 15.11 Entropy

Entropy, like internal energy, is a function of the state of the system.

$$\Delta S = \left( \frac{Q}{T} \right)_R$$

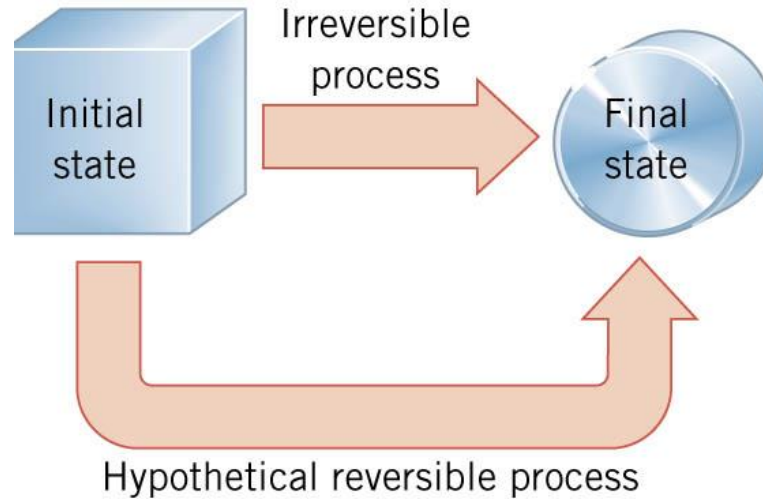
Consider the entropy change of a Carnot engine. The entropy of the hot reservoir decreases and the entropy of the cold reservoir increases.

$$\Delta S = +\frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} = 0$$

***Reversible processes do not alter the entropy of the universe.***

## 15.11 Entropy

What happens to the entropy change of the universe in an *irreversible process* is more complex.

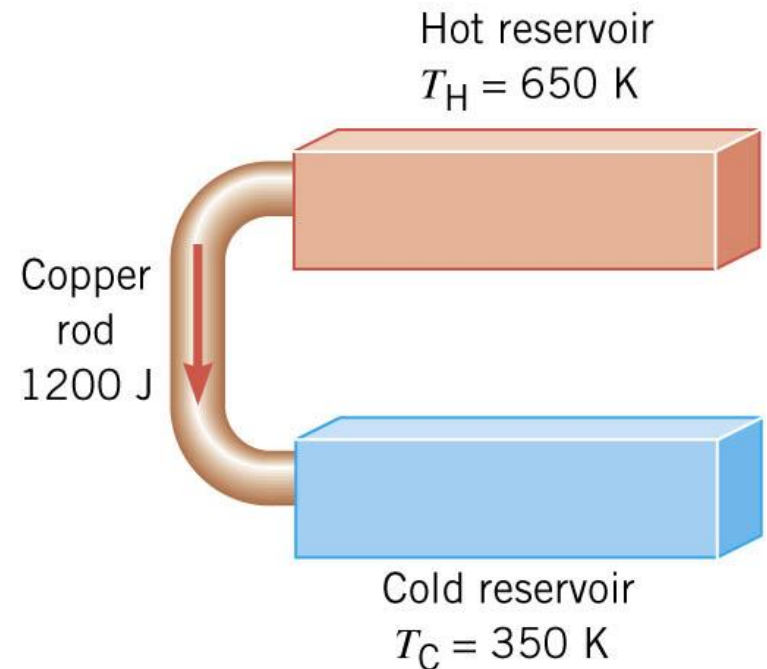


$$\Delta S \text{ for irreversible process} = \Delta S \text{ for hypothetical reversible process}$$

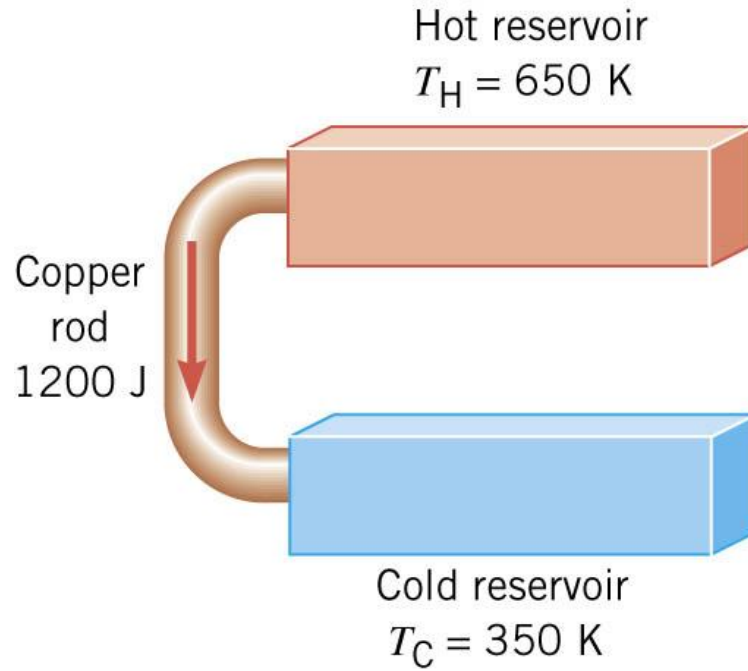
## 15.11 Entropy

### **Example 11 The Entropy of the Universe Increases**

The figure shows 1200 J of heat spontaneously flowing through a copper rod from a hot reservoir at 650 K to a cold reservoir at 350 K. Determine the amount by which this process changes the entropy of the universe.



## 15.11 Entropy



$$\Delta S_{\text{universe}} = +\frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} = +\frac{1200 \text{ J}}{350 \text{ K}} - \frac{1200 \text{ J}}{650 \text{ K}} = +1.6 \text{ J/K}$$



## 15.11 Entropy

*Any irreversible process increases the entropy of the universe.*

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

### THE SECOND LAW OF THERMODYNAMICS STATED IN TERMS OF ENTROPY

The total entropy of the universe does not change when a reversible process occurs and increases when an irreversible process occurs.

## 15.11 Entropy

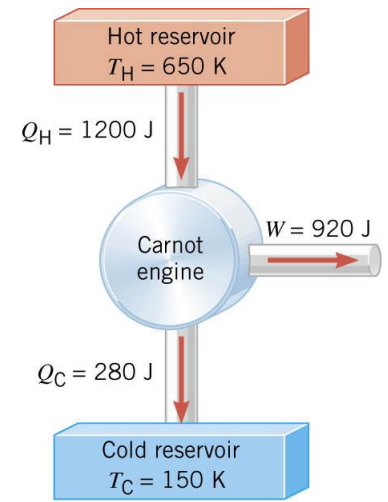
### Example 12 Energy Unavailable for Doing Work

Suppose that 1200 J of heat is used as input for an engine under two different conditions (as shown on the right).

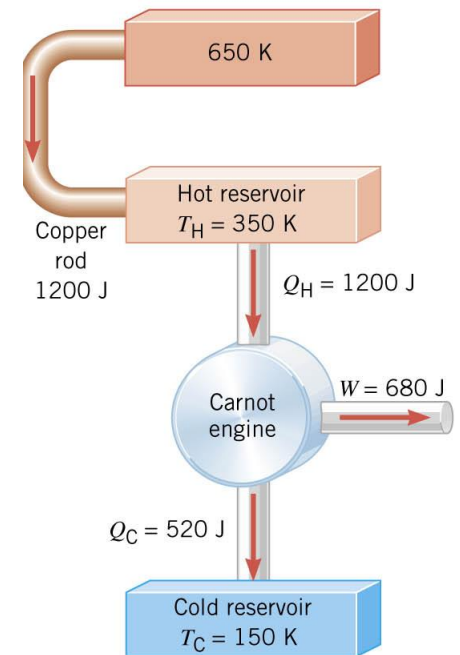
Determine the maximum amount of work that can be obtained for each case.

$$e_{\text{carnot}} = 1 - \frac{T_C}{T_H}$$

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



(a)



(b)

## 15.11 Entropy

The maximum amount of work will be achieved when the engine is a Carnot Engine, where

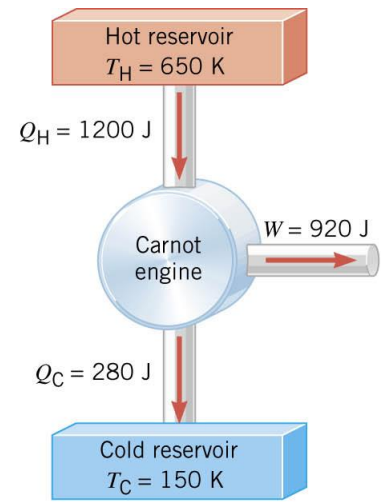
$$(a) \quad e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{150 \text{ K}}{650 \text{ K}} = 0.77$$

$$|W| = (e_{\text{carnot}}) |Q_H| = (0.77)(1200 \text{ J}) = 920 \text{ J}$$

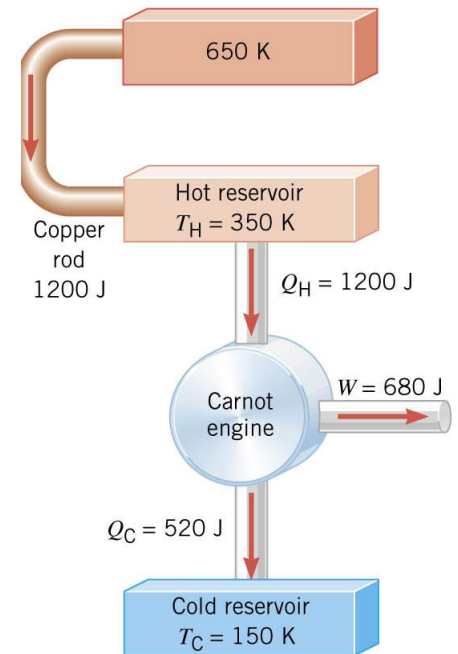
$$(b) \quad e_{\text{carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{150 \text{ K}}{350 \text{ K}} = 0.57$$

$$|W| = (e_{\text{carnot}}) |Q_H| = (0.57)(1200 \text{ J}) = 680 \text{ J}$$

The irreversible process of heat through the copper rod causes some energy to become unavailable.



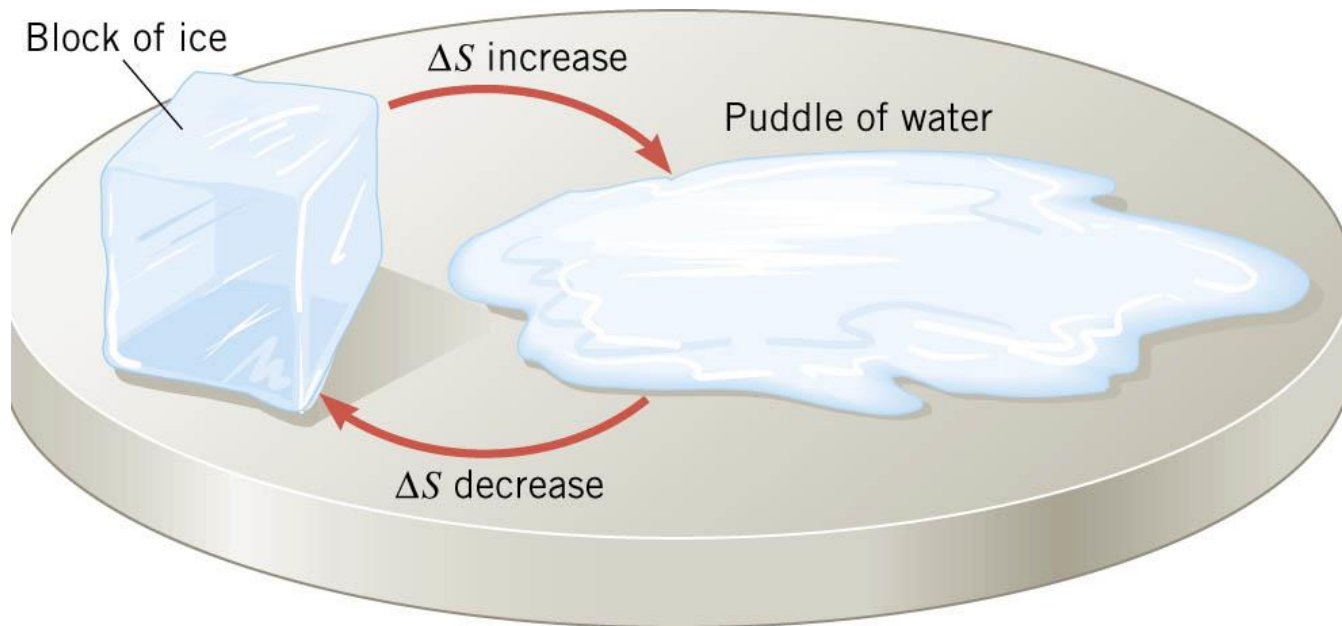
(a)



(b)

## 15.11 Entropy

$$W_{\text{unavailable}} = T_o \Delta S_{\text{universe}}$$



## 15.12 *The Third Law of Thermodynamics*

### THE THIRD LAW OF THERMODYNAMICS

It is not possible to lower the temperature of any system to absolute zero in a finite number of steps.