Chapter 18 First Law of Thermodynamics
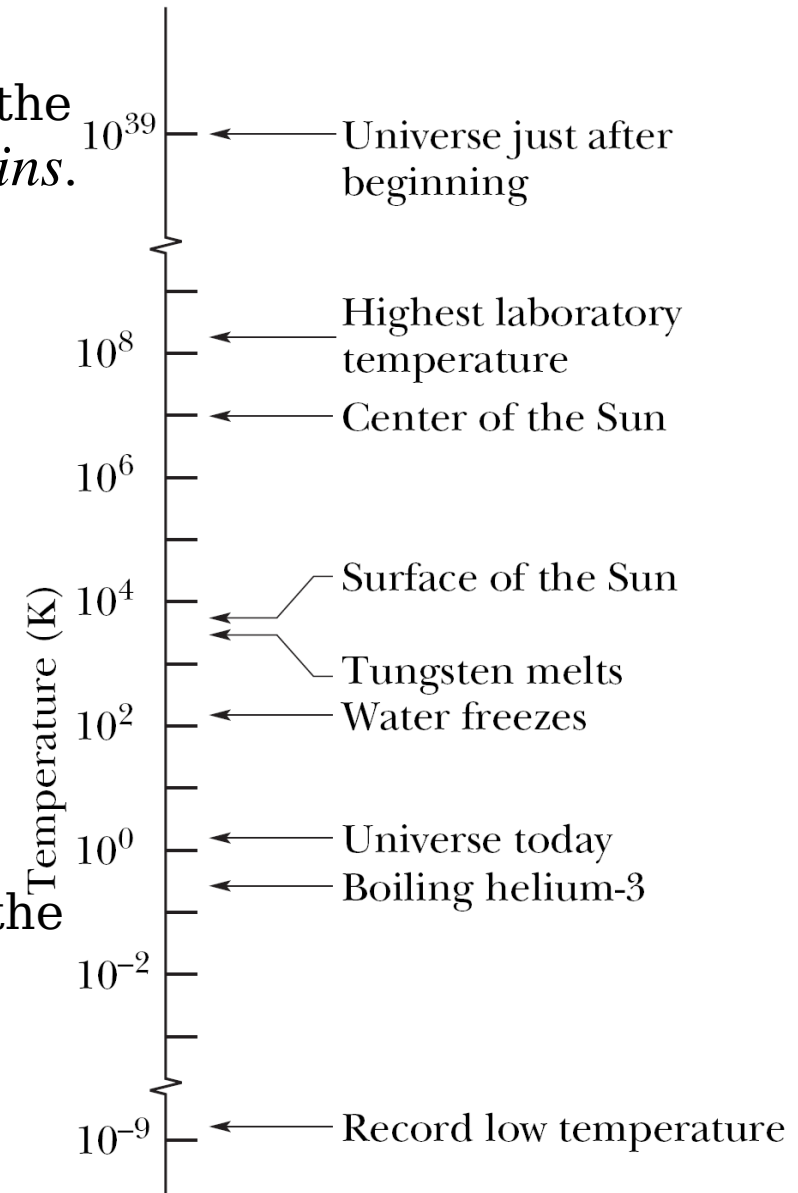
Thermodynamics: the study and application of the thermal energy (*internal energy*) of the systems.

Temperature

- Temperature: a SI base quantity, measured on the Kelvin scale in science, with the units called *kelvins*.

- this limiting low temperature is the zero of the Kelvin temperature scale, called *absolute zero*.

- Room temperature is about 290 kelvins.

The 0th Law of Thermodynamics

- The properties of many bodies change as we alter their temperature, We can use these properties as the basis of an instrument to know the concept of temperature.

- A **thermoscope**: The numbers increase when the device is heated and decrease when it is cooled.

Temperature (K)

10^{39} — Universe just after beginning

— Highest laboratory temperature

10^8

— Center of the Sun

10^6

10^4 — Surface of the Sun

— Tungsten melts

10^2 — Water freezes

10^0 — Universe today

— Boiling helium-3

10^{-2}

10^{-9} — Record low temperature

- Assume the number displayed for bodies T and A reach a stable, unchanging value. Then we say that the 2 bodies are in *thermal equilibrium* with each other. And bodies T and A must be at the same temperature.

- Assume bodies T and B come to thermal equilibrium at the same reading of the thermoscope. Then bodies T and B must be at the same temperature.

- If we now put bodies A and B into intimate contact they will be immediately in thermal equilibrium with each other.

0th law of thermodynamics:

If bodies A and B are each in thermal equilibrium with a 3rd body T, then A and B are in thermal equilibrium with each other.

- Every body has a property called **temperature**. When 2 bodies are in thermal equilibrium, their temperatures are equal. And vice versa
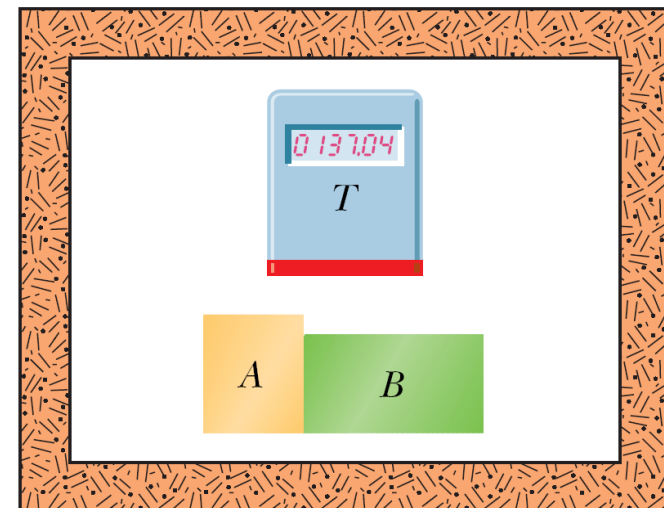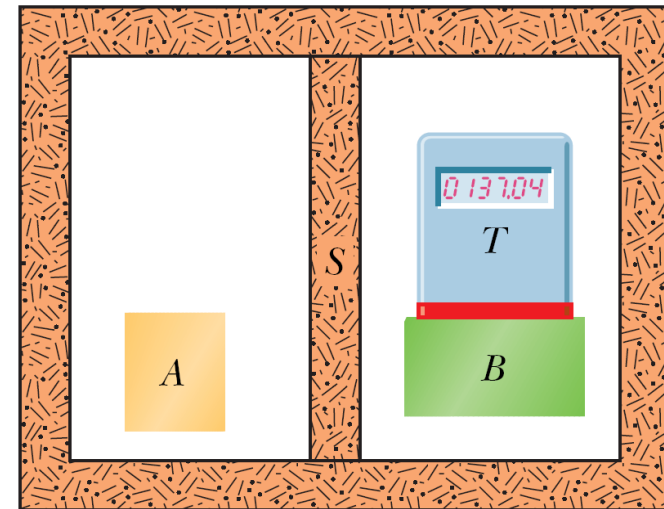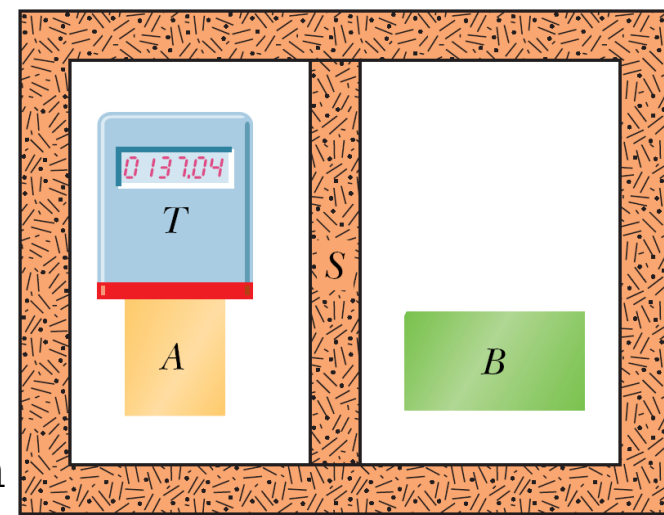
Measuring Temperature

The Triple Point of Water

● To set up a temperature scale, we pick some reproducible thermal phenomenon and we select a standard fixed point and give it a standard fixed-point temperature.

● the **triple point of water**: Liquid water, solid ice, and water vapor can coexist, in thermal equilibrium, at only one set of values of pressure and temperature.

● The triple point of water has been assigned a value of 273.16 K as the standard fixed-point temperature for the calibration of thermometers,

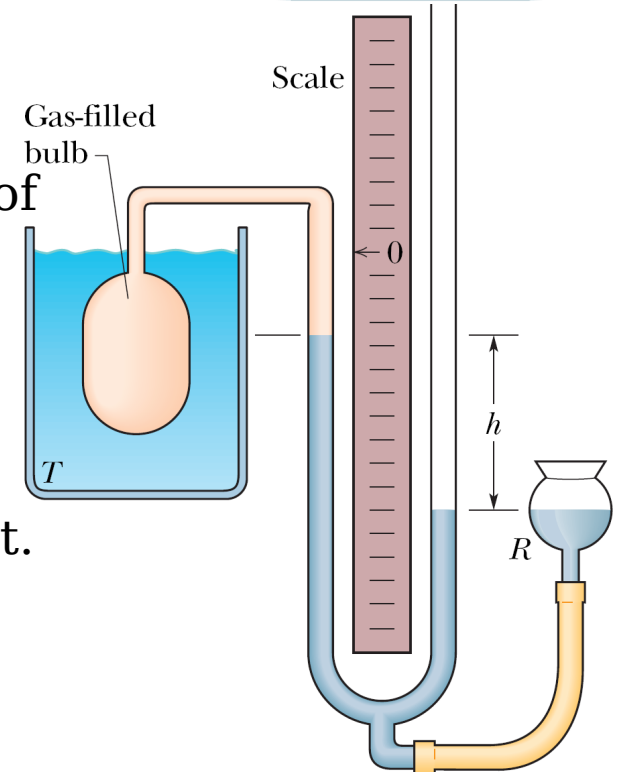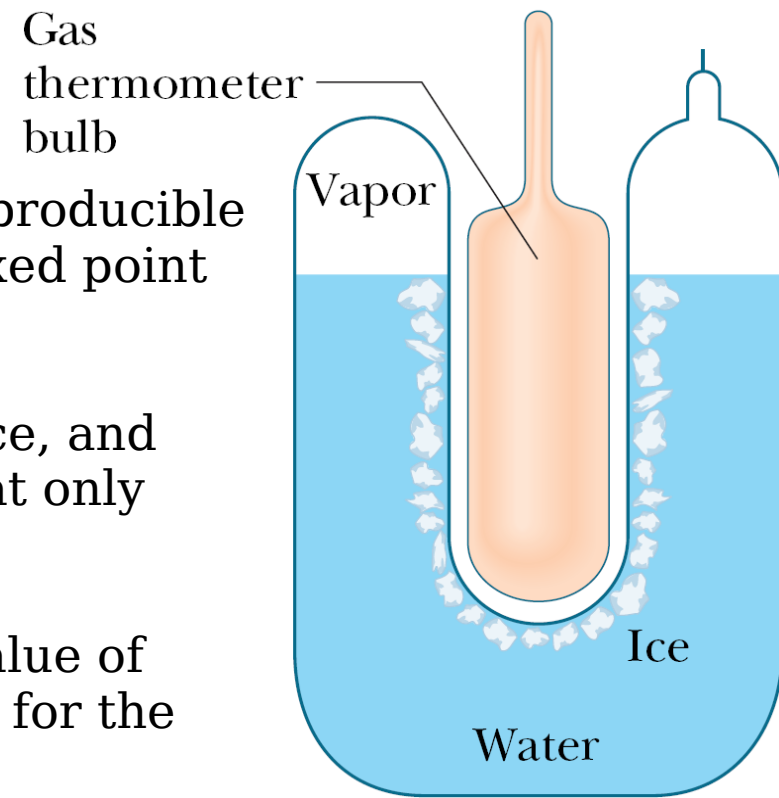$$T_3 = 273.16 \text{ K} \quad (\text{triple-point temperature})$$

The Constant-Volume Gas Thermometer

● The standard thermometer is based on the pressure of a gas in a fixed volume.

● The temperature of any body in thermal contact with the bulb is defined to be

$$T = C \, p$$

p is the pressure exerted by the gas and C is a constant.

Gas thermometer bulb

Vapor

Ice

Water

Scale

Gas-filled bulb

T

0

h

R

- the pressure p is $p = p_0 - \rho g h$, p_0 is the atmospheric pressure, ρ is the density of the mercury in the manometer

- If we next put the bulb in a triple-point cell, the temperature now being measured is $T_3 = C p_3$, p_3 is the gas pressure now.

- Eliminating C gives us the temperature as

$$T = T_3 \frac{p}{p_3} = (273.16 \text{ K}) \frac{p}{p_3} \quad \text{provisional}$$

- Different gases in the bulb give slightly different results.
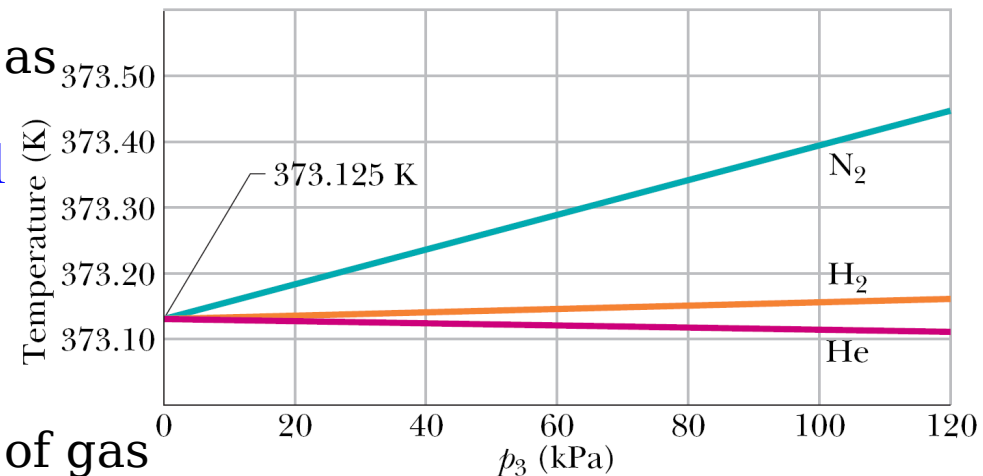
- As we use smaller and smaller amounts of gas to fill the bulb, the readings converge nicely to a single temperature, no matter what gas we use.

- Thus the recipe for measuring a temperature with a gas thermometer is

$$T = (273.16 \text{ K}) \lim_{\text{gas} \to 0} \frac{p}{p_3}$$

- The temperature obtained with the recipe is called the *ideal gas temperature*.

The Celsius and Fahrenheit Scales

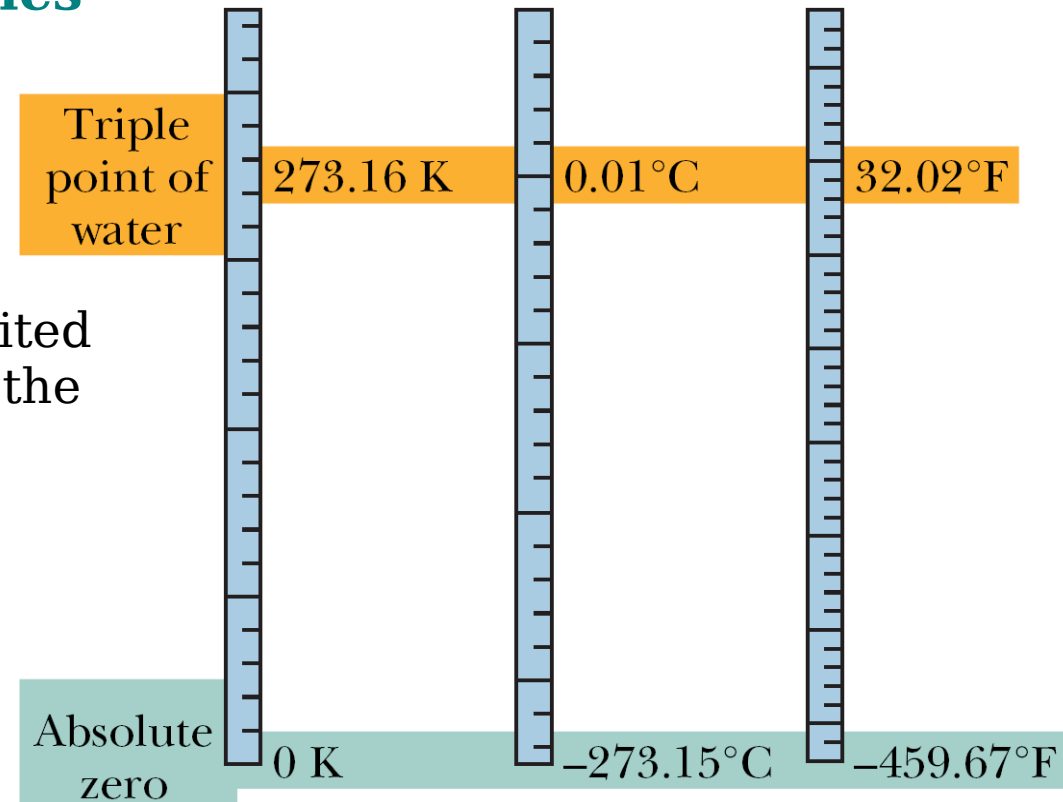● Celsius temperatures are measured in degrees, and the Celsius degree has the same size as the kelvin,

$$T_C = T - 273.15\ °$$

● The Fahrenheit scale, used in the United States, employs a smaller degree than the Celsius scale and a different zero of temperature,

$$T_F = \frac{9}{5} T_C + 32\ °$$

Triple point of water	273.16 K	0.01°C	32.02°F
Absolute zero	0 K	−273.15°C	−459.67°F

Some Corresponding Temperatures

Temperature	C	F
Boiling point of water	100	212
Normal body temperature	37.0	98.6
Accepted comfort level	20	68
Freezing point of water	0	32
Zero of Fahrenheit scale	$\simeq -18$	0
Scales coincide	−40	−40

● $$0\ °C = 32\ °F$$

means that 0° on the Celsius scale measures the same temperature as 32° on the Fahrenheit scale,

● $$5\ C° = 9\ F°$$

means that a temperature difference of 5 Celsius degrees is equivalent to a temperature difference of 9 Fahrenheit degrees.

Thermal Expansion

- **Thermal expansion** of materials with an increase in temperature is common in many situations: bridge, railroad, etc.

- The thermal expansion properties of some materials can be put to common use: thermometers using a *bi-metal strip*, or liquid-in-glass thermometers.
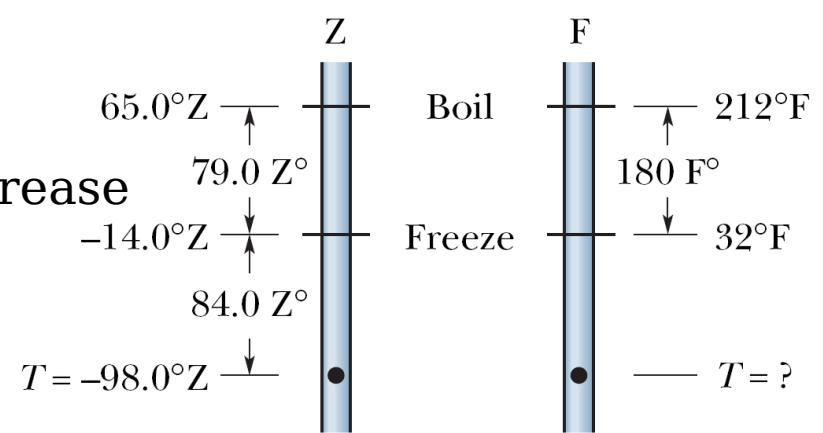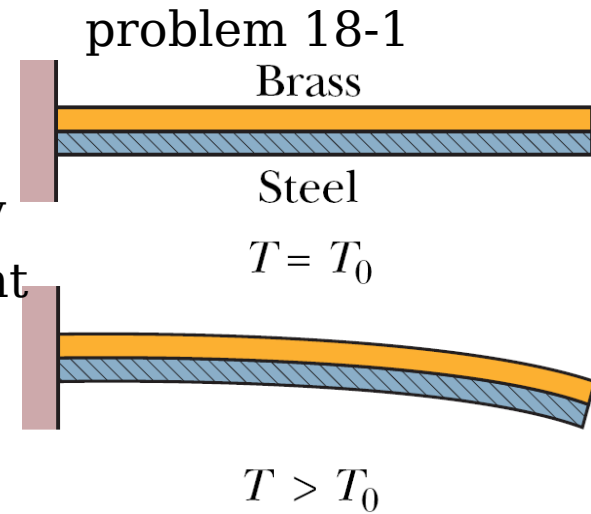
Linear Expansion

- If the temperature of a metal rod of length L is raised by an amount ΔT, its length is found to increase by an amount in which α is a constant called the **coefficient of linear expansion**.

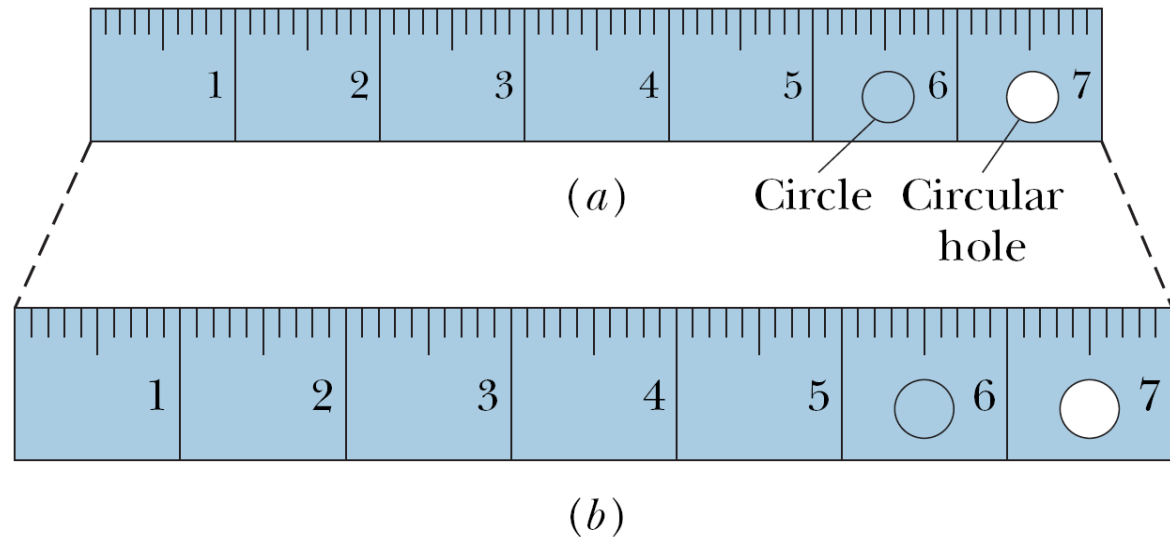$$\Delta L = L \, \alpha \, \Delta T$$

Volume Expansion

- If the temperature of a solid or liquid whose volume is V is increased by an amount ΔT, the increase in volume is

$$\Delta V = V \, \beta \, \Delta T$$

where β is the **coefficient of volume expansion**.

65.0°Z — Boil — 212°F
79.0 Z° — 180 F°
−14.0°Z — Freeze — 32°F
84.0 Z°
$T = -98.0°Z$ — $T = ?$

Z   F

problem 18-1

Brass
Steel
$T = T_0$

$T > T_0$

(a)   Circle Circular hole

1 2 3 4 5 6 7

(b)

1 2 3 4 5 6 7

$$L \quad \Rightarrow \quad L\,' = L + \Delta L = L\left(1 + \alpha\,\Delta T\right) \quad \Leftarrow \quad \Delta L = L\,\alpha\,\Delta T$$

$$V \quad \Rightarrow \quad V\,' = V + \Delta V = V\left(1 + \beta\,\Delta T\right) \quad \Leftarrow \quad \Delta V = V\,\beta\,\Delta T$$

$$V = L^3 \quad \Rightarrow \quad V\,' = L\,'^3 = L^3\left(1 + \alpha\,\Delta T\right)^3$$

$$= V\left[1 + 3\,\alpha\,\Delta T + 3\left(\alpha\,\Delta T\right)^2 + \left(\alpha\,\Delta T\right)^3\right]$$

$$\approx V\left(1 + 3\,\alpha\,\Delta T\right) = V + \Delta V$$

$$\Rightarrow \quad \beta = 3\,\alpha$$

- The coefficients of volume expansion and linear expansion for a solid are related by

$$\beta = 3\,\alpha$$

- However, water does not behave like other liquids:

  For $T > 4°C$: water expands as the temperature rises;
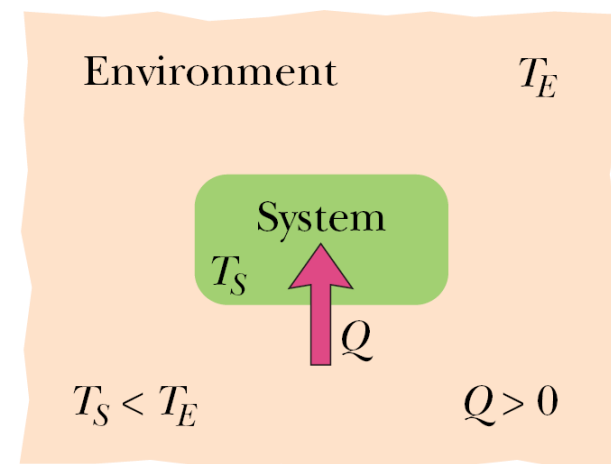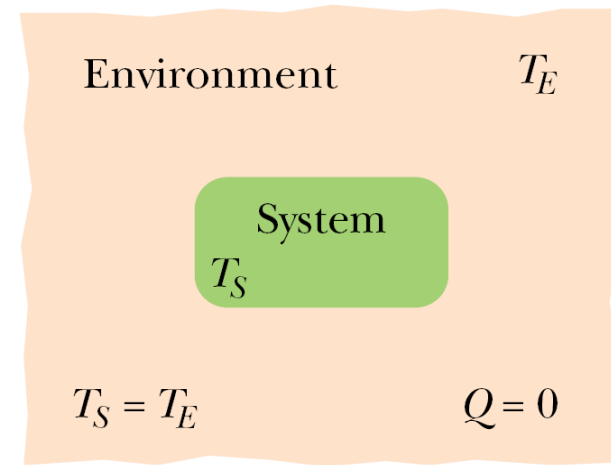 For $0 < T < 4°C$: water *contracts* with increasing temperature.
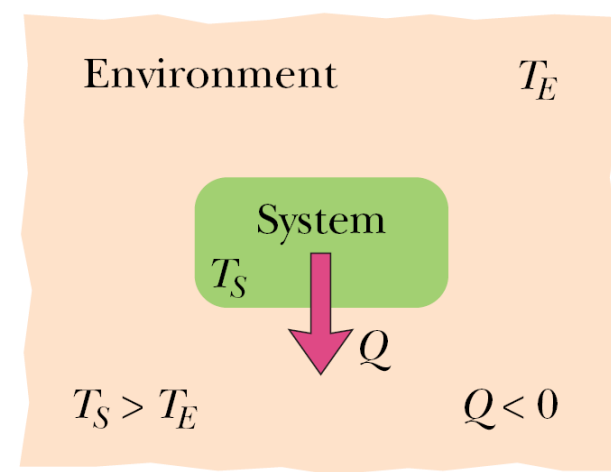
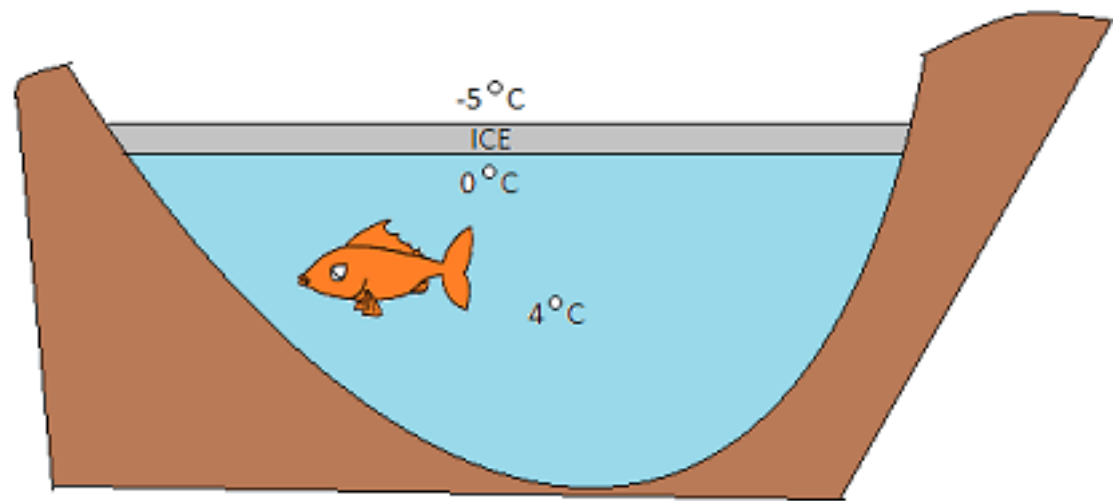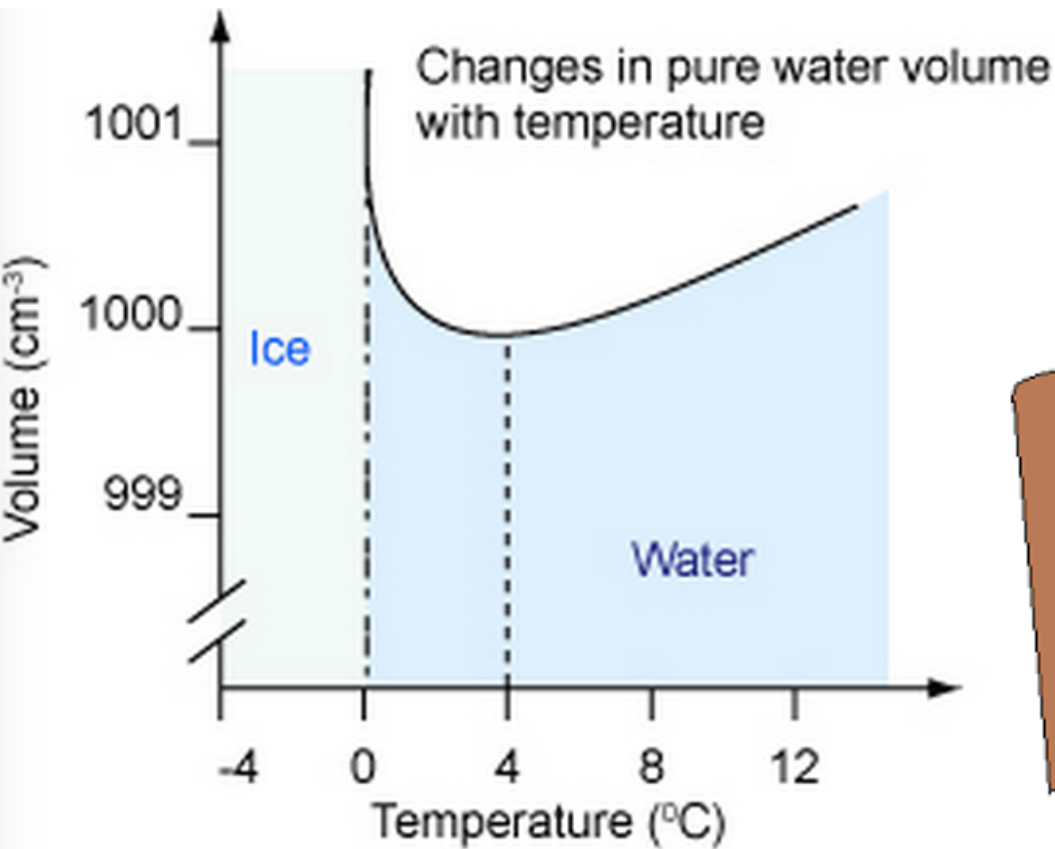- Thus, at about 4°C, the density of water passes through a maximum.

- This behavior of water is the reason lakes freeze from the top down rather than from the bottom up.

Problem 18-2

Temperature and Heat

- For a system with temperature T_S and its environment with temperature T_E, our observation is that if T_S is not equal to T_E, then T_S will change (T_E can also change some) until the 2 temperatures are equal and thus thermal equilibrium is reached.

Environment T_E

System

T_S

Q

$T_S > T_E$ $Q < 0$

Environment T_E

System

T_S

$T_S = T_E$ $Q = 0$

Environment T_E

System

T_S

Q

$T_S < T_E$ $Q > 0$

Changes in pure water volume with temperature

Maximum density at 3.98 °C = 39.2 °F
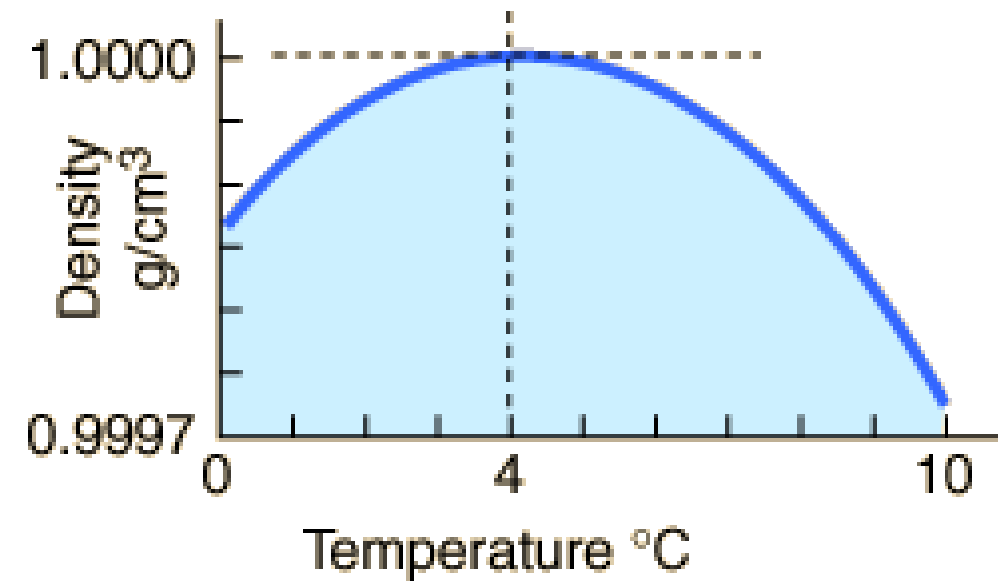
- Such a change in temperature is due to a change in the thermal energy of the system because of a transfer of energy between the system and its environment.

- The transferred energy is called **heat** (Q).

- Heat is *positive* when energy is transferred to a system's thermal energy from its environment. Heat is *negative* when energy is transferred from a system's thermal energy to its environment.

> Heat is the energy transferred between a system and its environment because of a temperature difference that exists between them.

- the **calorie** (cal) was defined as the amount of heat that would raise the temperature of $1g$ of water from 14.5°C to 15.5°C.

- the **British thermal unit** (Btu) is defined as the amount of heat that would raise the temperature of 1lb of water from 63°F to 64°F.

$$1\,\text{cal} = 3.969 \times 10^{-3}\,\text{Btu} = 4.1868\,\text{J}\,(\text{joule})$$

- The "calorie" used in nutrition, sometimes called the Calorie (Cal), is really a kilocalorie.

The Absorption of Heat by Solids and Liquids

Heat Capacity

- The heat capacity C of an object is the proportionality constant between the heat Q that the object absorbs or loses and the resulting temperature change T of the object

$$Q = C \, \Delta T = C \left(T_f - T_i \right)$$

- Heat capacity C has the unit of energy per degree or energy per kelvin.

Specific Heat

- 2 objects made of the same material will have different heat capacities proportional to their masses.

- It is convenient to define a "heat capacity per unit mass" or **specific heat** c that refers not only to an object but also to a unit mass of this material;

$$Q = c \, m \, \Delta T = c \, m \left(T_f - T_i \right)$$

- the specific heat of water is $c = 1 \, \text{cal}/\text{g} \cdot \text{C}^\circ = 1 \, \text{Btu}/\text{lb} \cdot \text{F}^\circ = 4190 \, \text{J}/\text{kg} \cdot \text{K}$

Molar Specific Heat

- $1 \, \text{mol} = 6.02 \times 10^{23}$ elementary units

- **molar specific heats**: specific heats involves moles.

An Important Point
● In determining and then using the specific heat of any substance, we need to know the conditions under which energy is transferred as heat, eg, constant pressure or constant volume.

Heats of Transformation
● When energy is absorbed as heat by a solid or liquid, the temperature of the sample does not necessarily rise. Instead, the sample may change from one *phase*, or *state*, to another.

● Matter can exist in 3 common states: In the *solid state*, the *liquid state*, and the *gas state*.

● To *melt* a solid means to change it from the solid state to the liquid state. The process requires energy because the molecules of the solid must be freed from their rigid structure.

● To *freeze* a liquid to form a solid is the reverse of melting and requires that energy be removed from the liquid, so that the molecules can settle into a rigid structure.

● To *vaporize* a liquid means to change it from the liquid state to the vapor (gas) state. This process requires energy because the molecules must be freed from their clusters.

- *Condensing* a gas to form a liquid is the reverse of vaporizing; it requires that energy be removed from the gas, so that the molecules can cluster instead of flying away from one another.

- The amount of energy per unit mass that must be transferred as heat when a sample completely undergoes a phase change is called the **heat of transformation** L.

- When a sample of mass m completely undergoes a phase change, the total energy transferred is
$$Q = L\,m$$

- When the phase change is from liquid to gas or from gas to liquid, the heat of transformation is called the **heat of vaporization** L_V.

- $L_V = 539 \text{ cal}/\text{g} = 40.7 \text{ kJ}/\text{mol} = 2256 \text{ kJ}/\text{kg}$ for water

- When the phase change is from solid to liquid or from liquid to solid, the heat of transformation is called the **heat of fusion** L_F.

- $L_F = 79.5 \text{ cal}/\text{g} = 6.01 \text{ kJ}/\text{mol} = 333 \text{ kJ}/\text{kg}$ for water

problem 18-3, 18-4

A Closer Look at Heat and Work

● The procedure by which you change the system from its initial state to its final state is called a *thermodynamic* process.

● During such a process, energy may be transferred into the system from the thermal reservoir (positive heat) or vice versa (negative heat). Also, work can be done by the system to raise the loaded piston (positive work) or lower it (negative work).

● Assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium.

● Allow the gas to push the piston upward through a differential displacement $\mathrm{d}\vec{s}$ with an upward force $\vec{F}$. Since the displacement is tiny, we can assume that $\vec{F}$ is constant during the displacement

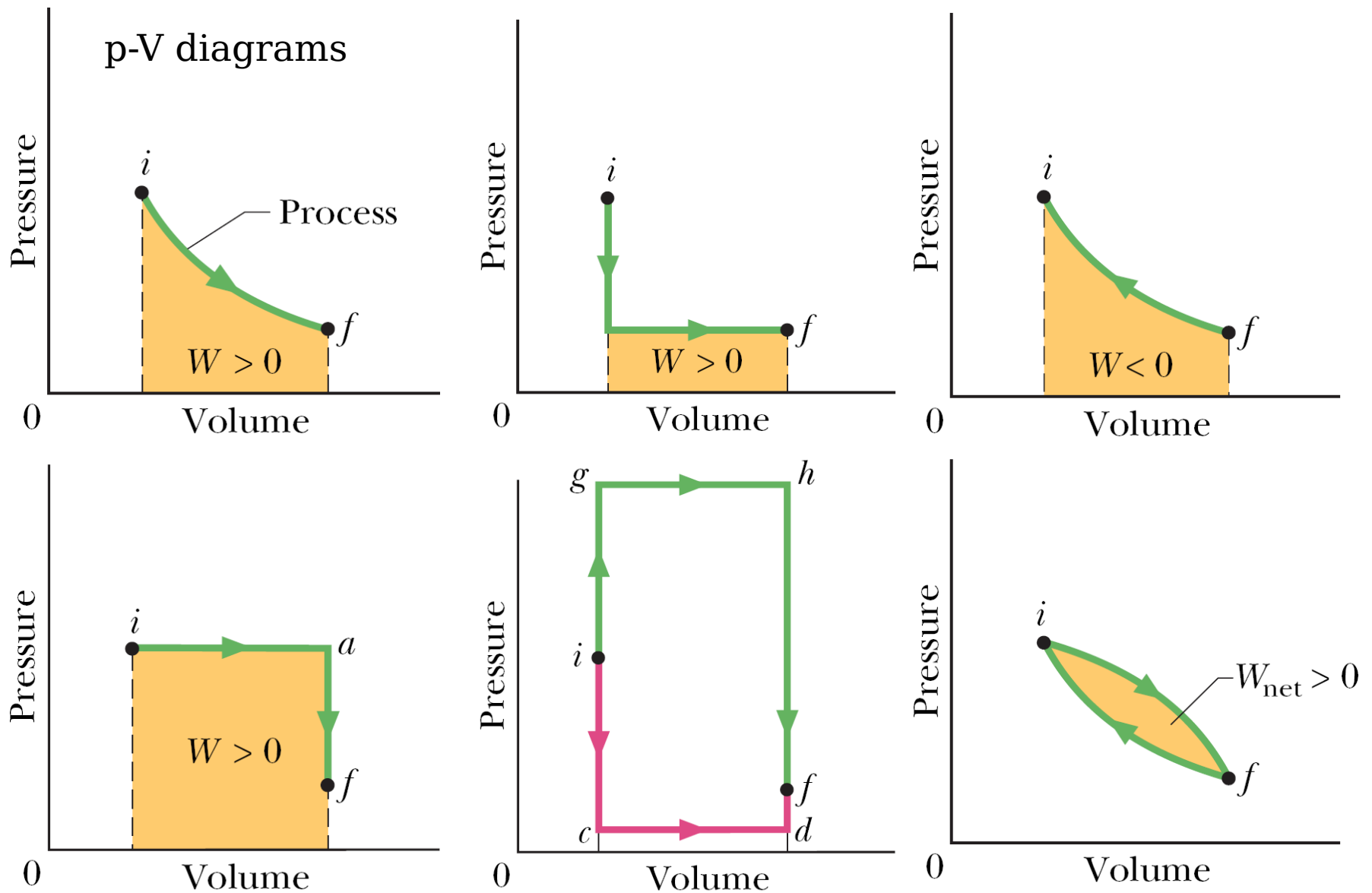$$\left|\vec{F}\right| = p\,A$$

● The differential work $\mathrm{d}W$ done by the gas during the displacement is

$$\mathrm{d}W = \vec{F}\cdot\mathrm{d}\vec{s} = \left(p\,A\right)\left(\mathrm{d}\,s\right) = p\left(A\,\mathrm{d}\,s\right) = p\,\mathrm{d}\,V$$

$$\boxed{W = \int \mathrm{d}\,W = \int_{V_i}^{V_f} p\,\mathrm{d}\,V}\quad \text{total work done by the gas .}$$

p-V diagrams
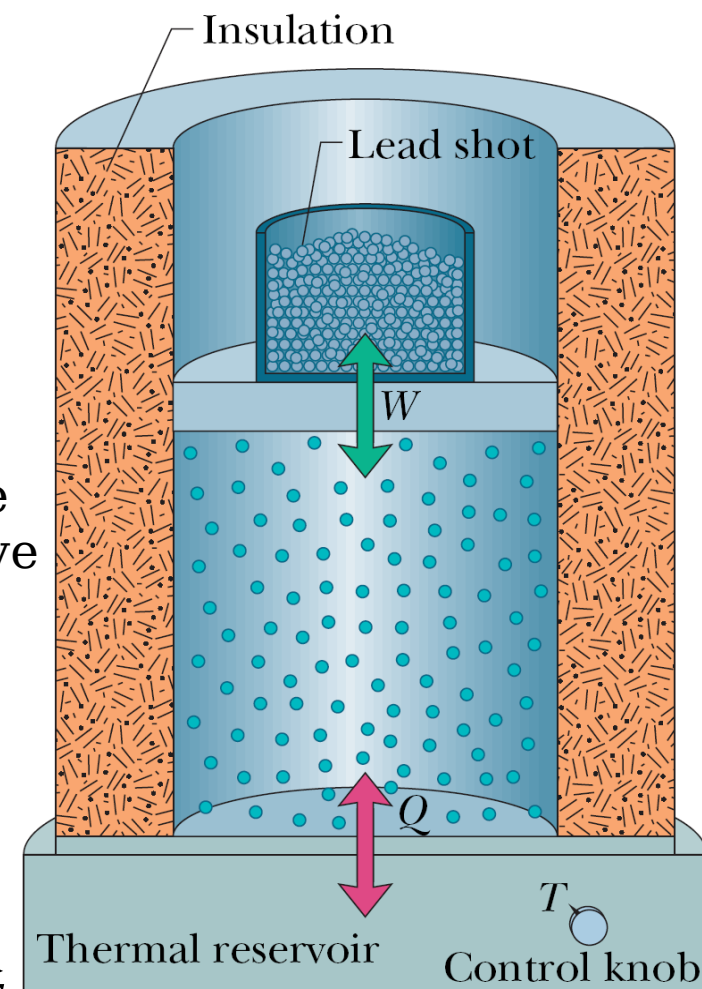
A system can be taken from a given initial state to a given final state by an infinite number of processes. The work W and the heat Q will have different values for different processes. We say that heat and work are *path-dependent* quantities.

The 1ˢᵗ Law of Thermodynamics

- Although the work W and the heat Q depend on the nature of the process. However, *the quantity $Q - W$ is the same for all processes*. It depends only on the initial and final states and does not depend on the path.

- We call this property the *internal energy* $\boxed{\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W}$ 1st law

It is the **1ˢᵗ law of thermodynamics**.

- The differential form $\boxed{d E_{\text{int}} = d Q - d W}$ 1st law

> The internal energy E_{int} of a system tends to increase if energy is added as heat Q and tends to decrease if energy is lost as work W done by the system.

- The 1ˢᵗ law of thermodynamics is an extension of the principle of energy conservation to systems that are *not* isolated. In such cases, energy may be transferred into or out of the system as either work W or heat Q.

- we assume that there are no changes in the kinetic energy or the potential energy of the system as a whole; i.e., $\Delta K = \Delta U = 0$.

- Notice the term *work W* about thermodynamics: the work done by a system is defined as being positive.

- The internal energy of a system tends to increase if
  (1) heat is absorbed by the system, or if
  (2) positive work is done on the system.

- The internal energy tends to decrease if
  (1) heat is lost by the system, or if
  (2) negative work is done on the system.

## Some Special Cases of the First Law of Thermodynamics

1. Adiabatic processes: An adiabatic process is one that occurs rapidly or occurs in a system that is insulated that *no transfer of energy as heat* occurs between the system and its environment, i.e., $Q = 0$, and the 1st law gives

$$\Delta E_{int} = -W \quad (\text{adiabatic process})$$

- In an idealized adiabatic process, the only way energy can be transferred between the system and its environment is by work.

2. Constant-volume processes: If the volume of a system is held constant, that system can do no work, i.e., $W = 0$, and the 1st law gives

$$\Delta E_{int} = Q \quad (\text{constant-volume process})$$
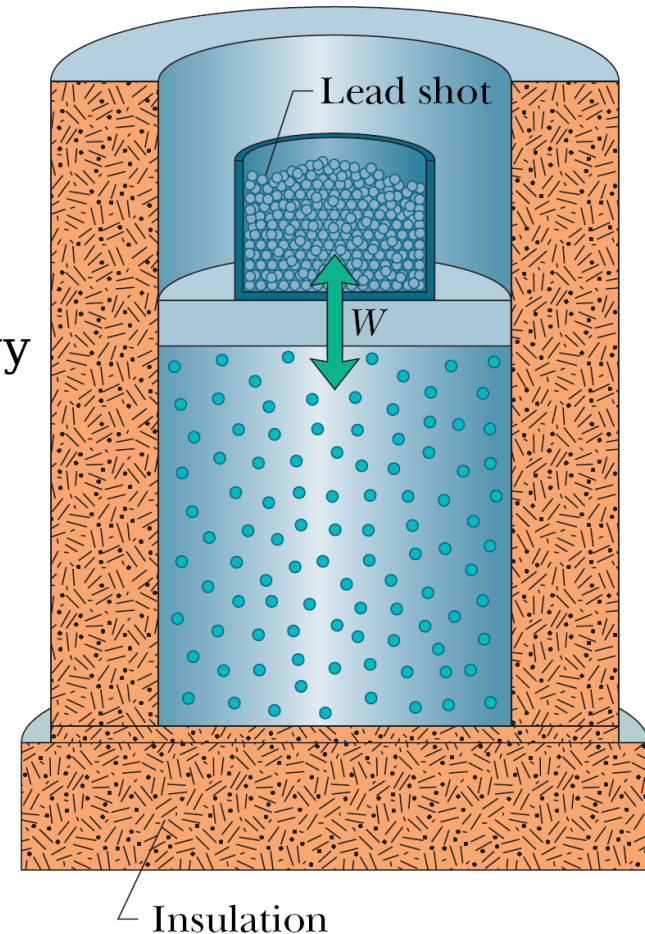
- if heat is absorbed by a system, the internal energy of the system increases. If heat is lost during the process, the internal energy of the system must decrease.

3. Cyclical processes: There are processes in which the system is restored to its initial state, i.e., $\Delta E_{int} = 0$, and the 1st law gives

$$Q = W \quad (\text{cyclical process})$$

- The net work done during the process must exactly equal the net amount of energy transferred as heat; the store of internal energy of the system remains unchanged.

4. Free expansions: These are adiabatic processes in which no transfer of heat occurs between the system and its environment and no work is done on or by the system, i.e., $Q = W = 0$, and the 1st law gives

$$\Delta E_{int} = 0 \quad (\text{free expansion})$$

- No heat is transferred to or from the gas because of the insulation. No work is done by the gas because it rushes into a vacuum and thus does not meet any pressure.
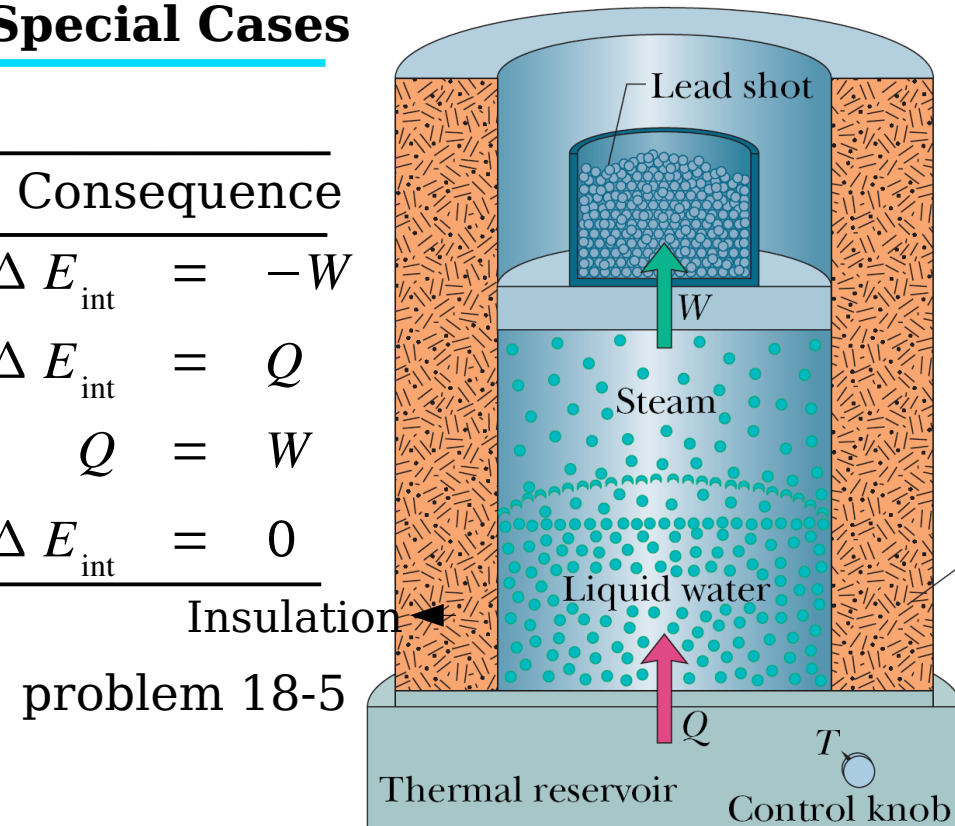
Stopcock

Vacuum

Insulation
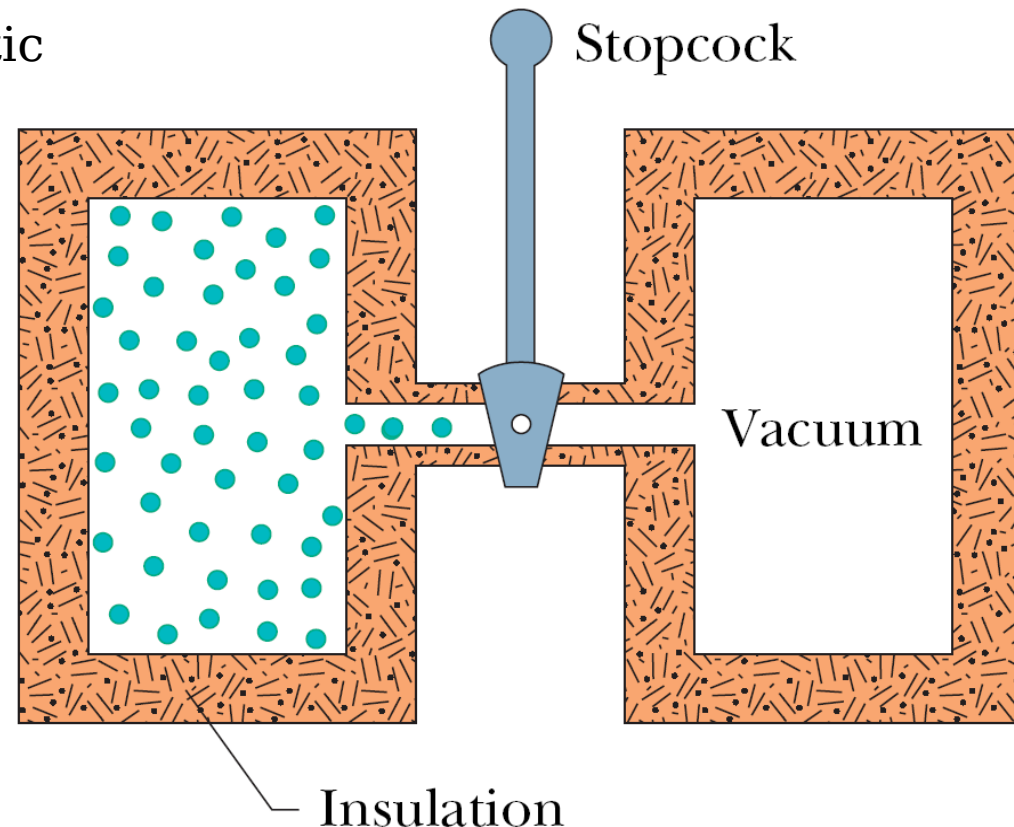
● During the sudden expansion, the gas is not in thermal equilibrium and its pressure is not uniform. We can plot the initial and final states on a p-V diagram, but we cannot plot the expansion itself.

The 1st Law of Thermodynamics: Four Special Cases

the law: $\Delta E_{int} = Q - W$

Process	Restriction		Consequence		
Adiabatic	Q = 0		ΔE_{int}	=	$-W$
Constant volume	W = 0		ΔE_{int}	=	Q
Closed cycle	ΔE_{int} = 0		Q	=	W
Free expansion	Q = W = 0		ΔE_{int}	=	0

Insulation ◄

problem 18-5

Lead shot
W
Steam
Liquid water
Q
T
Thermal reservoir
Control knob

Heat Transfer Mechanisms
● 3 transfer mechanisms: **conduction**, **convection**, and **radiation**.

Conduction
● Q is the energy that is transferred as heat through the slab, from its hot face to its cold face, in time t.

- the *conduction rate* P_{cond} (the amount of energy transferred per unit time) is

$$P_{\text{cond}} = \frac{Q}{t} = k\,A\,\frac{T_H - T_C}{L}$$

k is called the *thermal conductivity*.

## Thermal Resistance to Conduction (*R*-Value)

- the *thermal resistance R* of a slab of thickness L is defined as

$$R = \frac{L}{k}$$

- something that has a high R-value is a *poor thermal conductor* and thus a *good thermal insulator*.

Conduction Through a Composite Slab

- assume that the transfer is a *steady-state* process, i.e., the temperatures everywhere in the slab and the rate of energy transfer do not change with time.

- In the steady state, the energy transferred through one material in a certain time must be equal to that transferred through the other material in the same time.
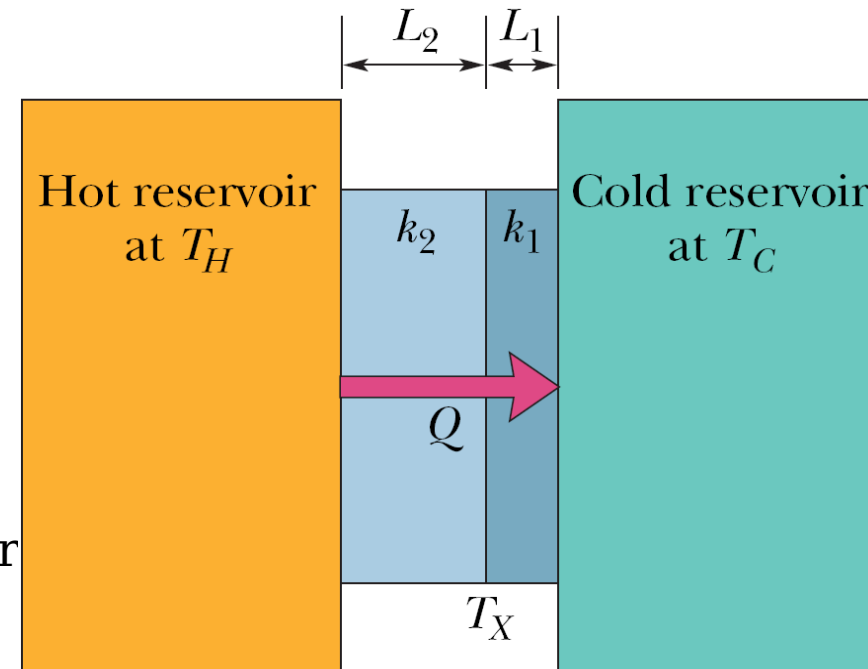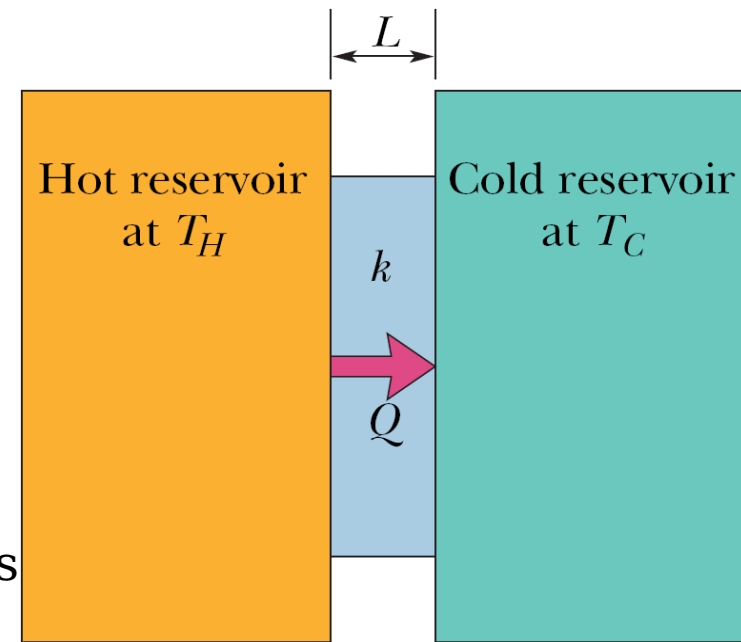
- Letting T_X be the temperature of the interface between the 2 materials, then

$$P_{cond} = k_2 A \frac{T_H - T_X}{L_2} = k_1 A \frac{T_X - T_C}{L_1} \quad \Rightarrow \quad T_X = \frac{k_1 L_2 T_C + k_2 L_1 T_H}{k_1 L_2 + k_2 L_1}$$

$$\Rightarrow \quad P_{cond} = A \frac{T_H - T_C}{L_1/k_1 + L_2/k_2}$$

- extend the equation to apply to any number n of materials making up a slab:

$$P_{cond} = A \frac{T_H - T_C}{\sum (L/k)}$$

The summation sign in the denominator means to add the values of L/k for all the materials.

Convection
- Such energy transfer occurs when a fluid comes in contact with an object whose temperature is different from that of the fluid.

- The temperature of the part of the fluid that is in contact with a hot object increases, and (in most cases) that fluid expands and thus becomes less dense. Because this expanded fluid is now lighter than the surrounding cooler fluid, buoyant forces cause it to rise. Some of the surrounding cooler fluid then flows to take the place of the rising warmer fluid, and the process then continue.

- Convection is part of many natural processes: atmosphere, ocean, sun, etc.

Radiation

- the **thermal radiation** exchanges energy as heat is via electromagnetic waves.

- No medium is required for heat transfer via radiation, i.e., the radiation can travel through vacuum.

- The rate P_{rad} at which an object emits energy via electromagnetic radiation depends on the object's surface area A and the temperature T of that area

$$P_{rad} = \sigma\, \varepsilon\, A\, T^4$$

- $\sigma = 5.6703 \times 10^{-8}\,\text{W/m}^2 \cdot \text{K}^4$ is called the *Stefan-Boltzmann constant*. ε represents the *emissivity* of the object's surface, which has a value between 0 and 1, depending on the composition of the surface.

- A surface with the maximum emissivity of 1 is a *blackbody radiator*, but such a surface is an ideal limit and does not occur in nature.

- A temperature of absolute 0 corresponds to no radiation. Every object whose temperature is above 0 K emits thermal radiation.
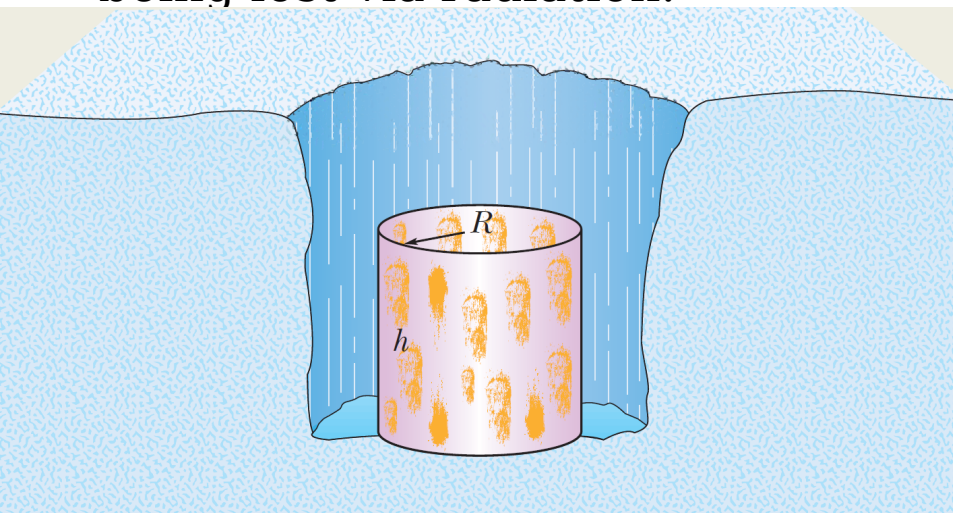
- The rate P_{abs} at which an object absorbs energy via thermal radiation from its environment,

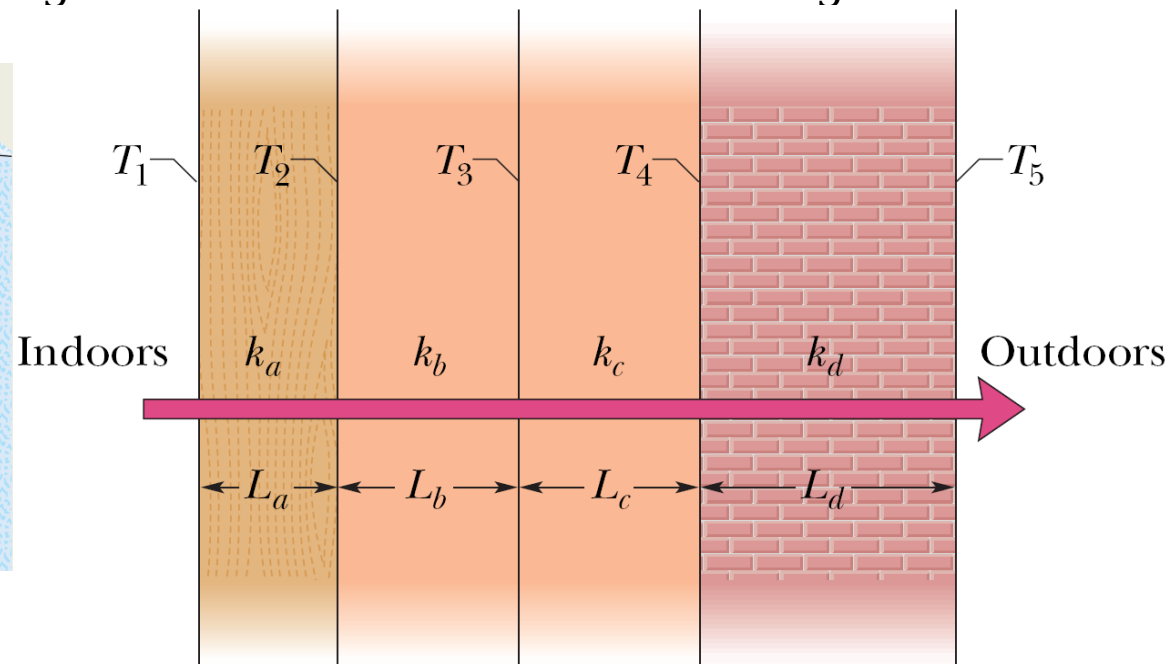$$P_{abs} = \sigma \, \varepsilon \, A \, T_{env}^4$$

- An object will radiate energy to the environment while it absorbs energy from the environment, its net rate P of energy exchange due net to thermal radiation is

$$P_{net} = P_{abs} - P_{rad} = \sigma \, \varepsilon \, A \left(T_{env}^4 - T^4 \right)$$

- P_{net} is positive if net energy is being absorbed via radiation and negative if it is being lost via radiation.

problem 18-7

problem 18-6

The chosen problems: 7, 14, 18, 54