Chapter18 Thermodynamics

Thermodynamics is the study of the thermal energy of the systems.
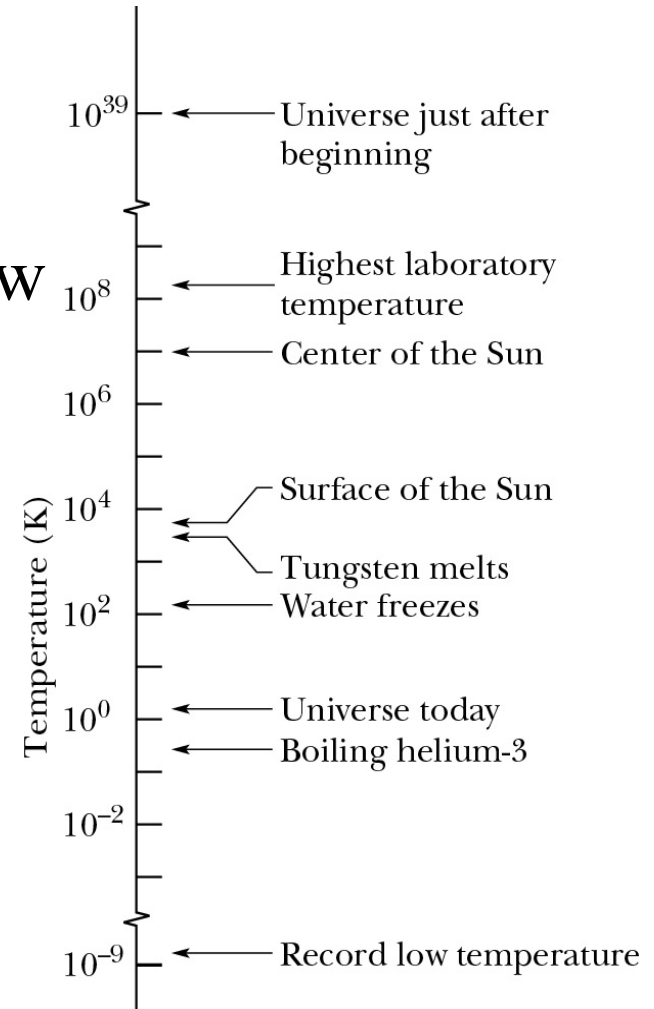
Need to define another parameter:
Temperature

Formal definition will come later, now let's become familar with it.

SI unit (nature's unit) for temperature: Kelvin (K)

room temperature: 290 K
water freezes: 273 K
absolute zero: 0 K

Temperature (K)

10^{39} — Universe just after beginning

10^{8} — Highest laboratory temperature

— 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

The Zeroth Law of Thermodynamics

Thermal equilibrium: Two bodies in contact come to a stable condition.

Zeroth law of thermodynamics: If bodies A and B are each in thermal equilibrium with a third body T, then they are in thermal equilibrium with each other.

Temperature is the property that determines whether one object is in thermal equilibrium with the other object.
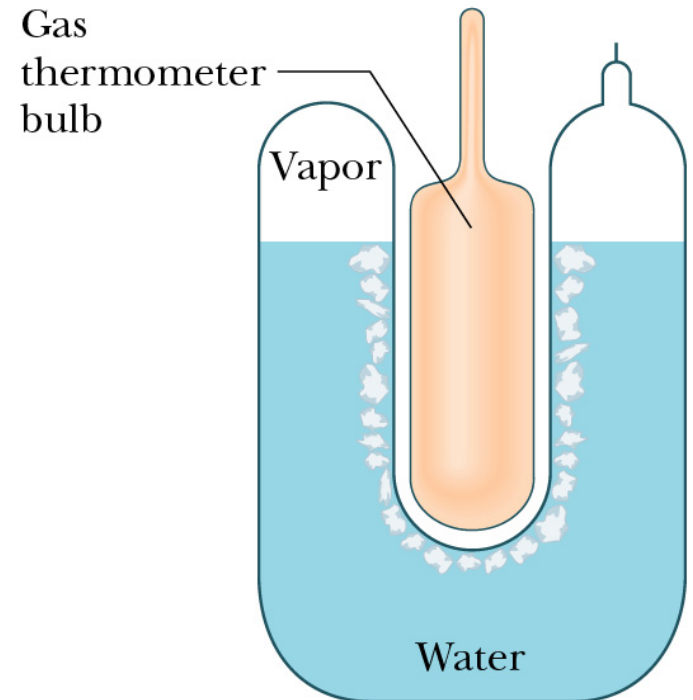
If $T_A = T_T$ and $T_B = T_T$ then $T_A = T_B$

Absolute temperature -- Kelvin

"Nature's" temperature scale

Triple point of water: water, ice and water vapor coexist in thermal equilibrium. It always occurs at a fixed temperature, T_3

assign $T_3 = 273.16$ K

1 Kelvin = 1/273.16 of the difference between the absolute zero and the triple-point temperature of water.

The constant volume gas thermometer

- when T increases, if V is kept constant, p increases
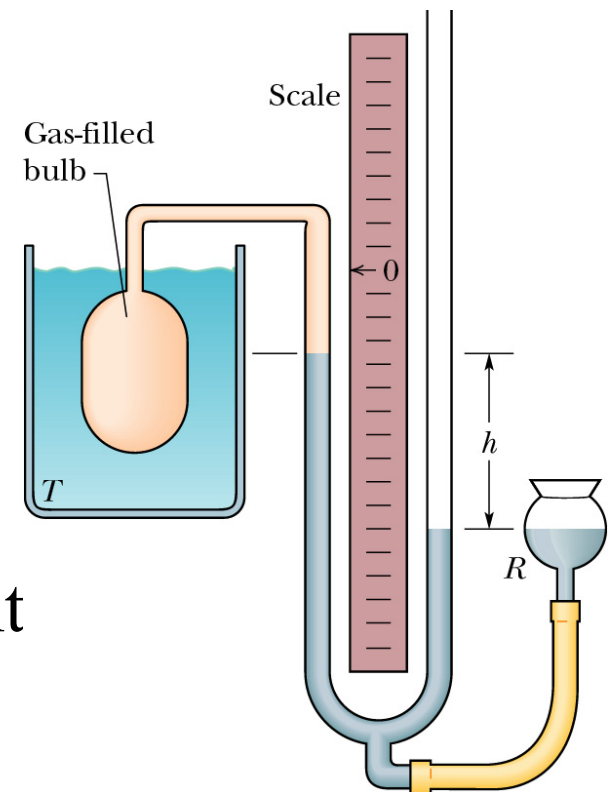 define $T = C\,p$ (C is a constant) $p = p_0 - \rho g h$
  Now, use it to measure a triple point cell:
  $T_3 = C\,p_3$
  so $T/T_3 = p/p_3$
  $T = (273.16\,K)(\,p/p_3\,)$
- At low pressure limit, T measured does not depend on the type of gas
- All other thermometers can be calibrated against such measurement

Scale

Gas-filled bulb

0

h

T

R

The Celsius and Fahrenheit scales

Celsius scale. Celsius degree has the same size as the Kelvin, but the zero point is different

$$T_C = (T_K - 273.15)^oC$$

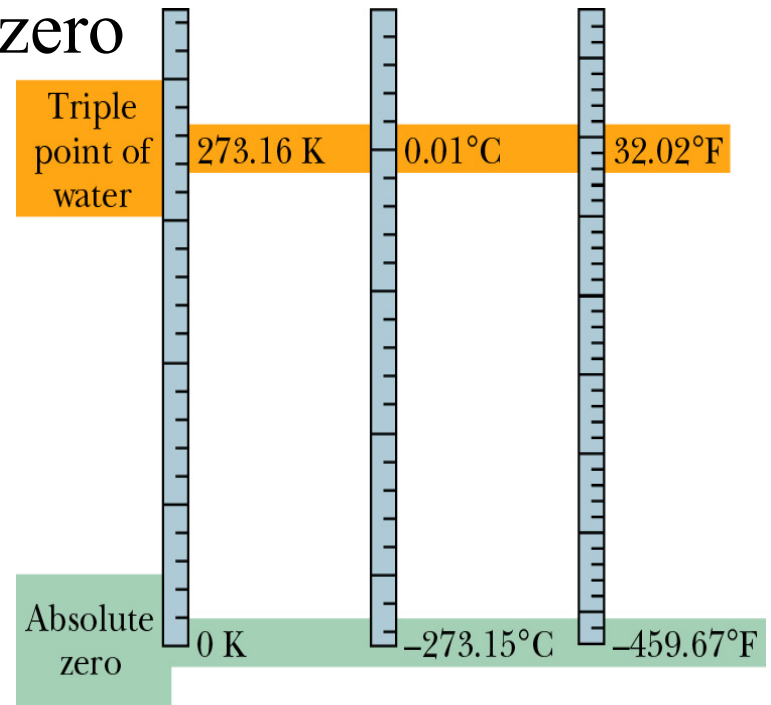**Fahrenheit scale**. Fahrenheit degree is smaller than Celsius degree, the zero point is also different

$$T_F = ((9/5) T_C + 32)^oF$$

Boiling point of water:

$$T_C = 100^oC, \ T_F = 212^oF$$

$$T_K = 373.15 \ K$$

Triple point of water: 273.16 K | 0.01°C | 32.02°F

Absolute zero: 0 K | −273.15°C | −459.67°F

Thermal Expansion

- Most objects expand when they are heated to a higher temperature

- **Linear expansion**.

  $\Delta L = \alpha\, L\, \Delta T$
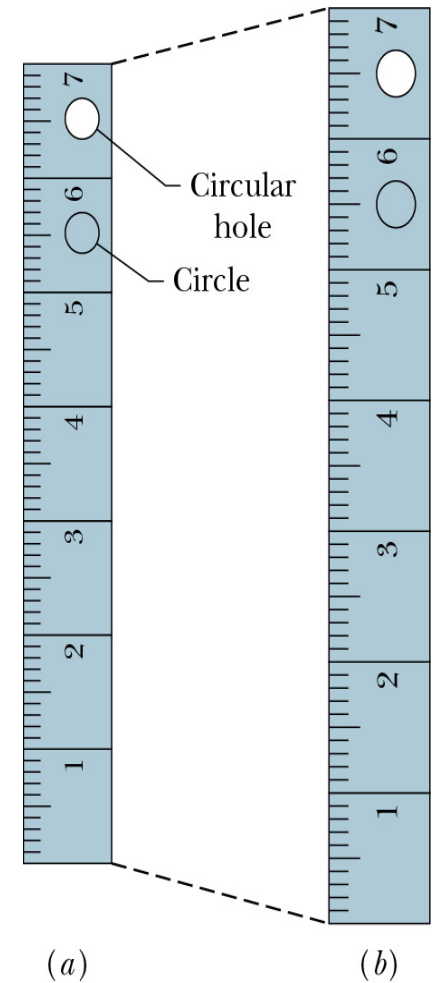
  α : coefficient of linear expansion,

  $\alpha = (\Delta L/L)/\Delta T$ unit: $1/K$, $1/^oC$

  α is different for different materials

  Al: $2.3 \times 10^{-5}/^oC$, steel: $1.1 \times 10^{-5}/^oC$,

  1 m long steel ruler, heated up 5^oC,

  $\Delta L = (1.1 \times 10^{-5}/^oC)(1m)(5^oC) = 5.5 \times 10^{-5}m$
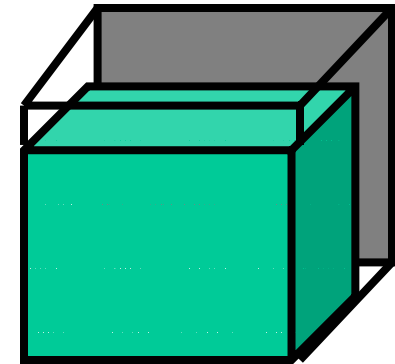
Circular hole
Circle

(a)   (b)

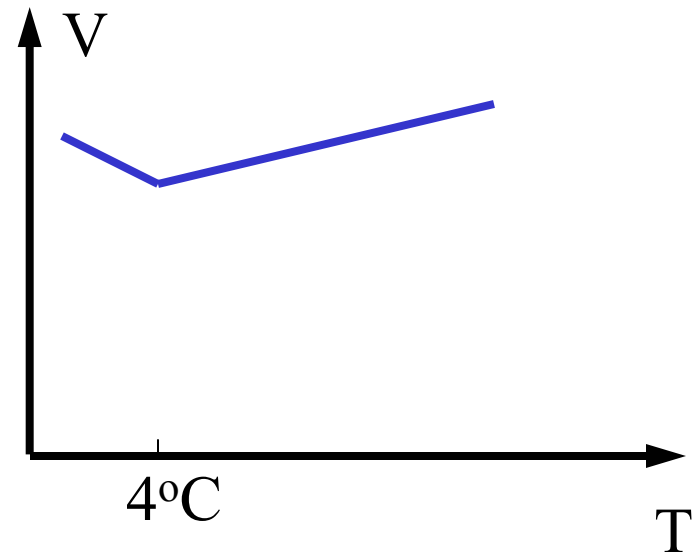- **Volume expansion**

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

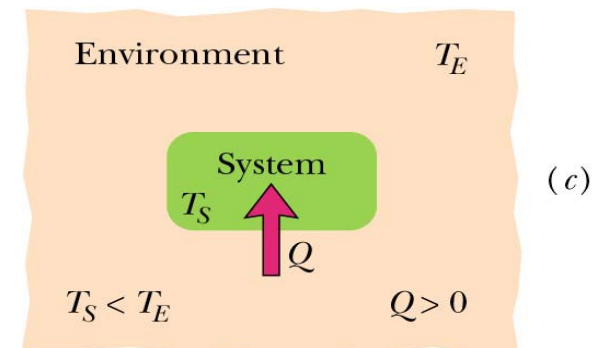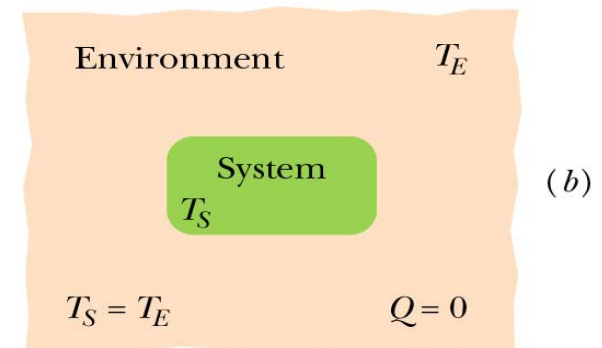β : coefficient of volume expansion

$$\beta = 3\alpha$$

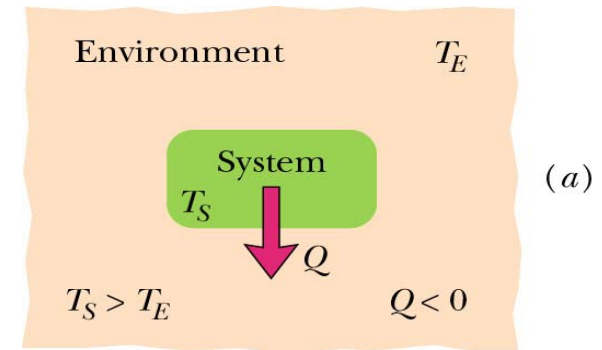- A special case: volume expansion of water: Why lakes freeze from the top down rather than from the bottom up?

V

4°C

T

Temperature and Heat

- If the temperatures of the system and its environment are not the same, energy is transferred between them. This transferred energy is called **heat (Q)**.

- If $T_S < T_E$, heat is transferred into system, Q positive

- If $T_S > T_E$, heat is transferred out of system, Q negative

- If $T_S = T_E$, no heat transfer takes place, Q = 0

Environment T_E

System

T_S

Q

$T_S > T_E$ $Q < 0$ (a)

Environment T_E

System

T_S

$T_S = T_E$ $Q = 0$ (b)

Environment T_E

System

T_S

Q

$T_S < T_E$ $Q > 0$ (c)

- **Heat** is **not an intrinsic** property of a system, but a physical property associated with a **process**. So is **work**.

- Unit of heat:
  - calorie(cal): heat needed to raise the temperature of 1 g of water for 1^oC (from 14.5^oC to 15.5^oC)

  - British thermal unit (BTU): heat needed to raise 1 lb water by 1^oF (from 63^oF to 64^oF)

  - 1 cal = 3.969 x10^{-3} Btu = 4.1860 J

  - "Calorie" in food labels: 1 Calorie(Cal) = 1000 calorie

The absorption of heat by solids and liquids

- **Heat capacity**: when the temperature of an object is raised from T_i to T_f, heat is absorbed:

    $Q = C (T_f - T_i)$

    The constant C is called the **heat capacity** of the object.

    Unit of C: energy/degree, e.g. J/K, cal/^{o}C

- **Specific heat**:

  - It takes more heat to raise same ΔT for a larger pot of water
  - Q is proportional to both $(T_f - T_i)$ and mass
    $$Q = c\, m\, (\, T_f - T_i\,)$$
  - c : **specific heat**, different for different materials
  - e.g, 1 cal is the heat to raise 1 ^{o}C for 1 g water:
    $c_{water} = Q/[m(T_f - T_i\,)] = 1$ cal/(1g $\cdot$1 ^{o}C) = 4190 J/(kg $\cdot$ K)
    $c_{Tungsten} = 134$ J/(kg $\cdot$ K) ; $c_{Al} = 900$ J/(kg $\cdot$ K)
  - Specific heat is heat capacity per unit mass
    $$C = m\, c$$

Checkpoint

A certain amount of heat Q will warm 1 g of material A by 3 °C and 1 g of material B by 4 °C. Which material has the greater specific heat?

$$Q = c_A \, m_A \Delta T_A = c_B \, m_B \Delta T_B$$

$$\Rightarrow \quad c_A = (m_B/m_A)(\Delta T_B / \Delta T_A) \, c_B$$

- **Molar specific heat**: heat capacity of 1 mol of substance.

  1 mol = 6.02 x10^{23} elementary units

  e.g. 1 mol of Al means 6.02 x10^{23} Al atoms

- Heat is a quantity associated with a process. Therefore, for specific heat, we need to specify the process. For example: constant–pressure process, constant-volume process, etc

Heat of Transformation: When ice melts or water boils, heat is absorbed, but T does not change. The system undergoes a phase transition.

$$Q = m\,L$$

m = mass, L = **Latent heat of transformation**.

Heat of vaporization L_V: For liquid vaporizing to gas, or gas condenses to liquid.

water, L_V = 539 cal/g = 2256 kJ/kg

Heat of fusion L_F: For solid melting to liquid, or liquid freezing to solid.

water, L_F = 79.5 cal/g = 333 kJ/kg

1.0 kg of ice at 0^oC is converted to steam of 100^oC. How much heat is needed?

For water: $c_w = 1,000$ cal/kg$\cdot^oC$

$L_F = 79,500$ cal/kg $L_V = 540,000$ cal/kg

First: Change ice into liquid water at 0^oC

$Q_F = m\,L_F = (1.0kg)(79500$ cal/kg$) = \boxed{79,500$ cal$}$

Second: Raise the temperature of the water from 0^oC to 100^oC

$Q_w = mc_w\,\Delta T = (1.0kg)(1000$ cal/kg$\cdot^oC)(100^oC) = \boxed{100,000$ cal$}$

Third: Change liquid water into steam at 100^oC

$Q_V = m\,L_V = (1.0kg)(540000$ cal/kg$) = \boxed{540,000$ cal$}$

Total heat required: $79,500 + 100,000 + 540,000 = 719,500$ cal

Heat and Work

Energy can be transferred as **heat** and **work** between a system and its environment.

To take a system from an initial state: p_i, V_i, T_i to a final state: p_f, V_f, T_f is called a **thermodynamic** process.
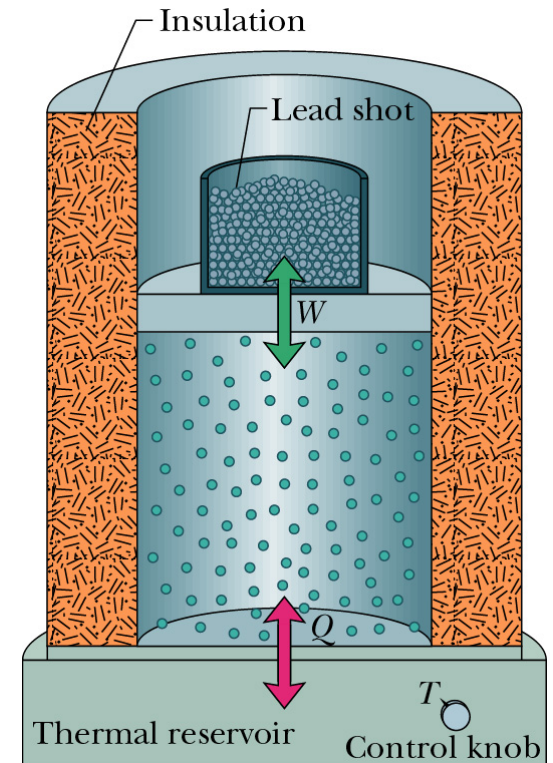
Work done by the gas on the piston:

$$dW = \vec{F} \cdot d\vec{s} = (pA)(ds) = p\,dV$$

From V_i to V_f:
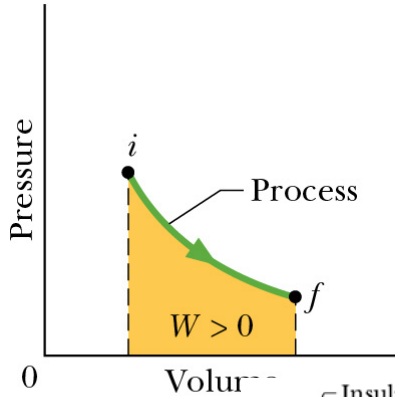
$$W = \int dW = \int_{V_i}^{V_f} p\,dV$$

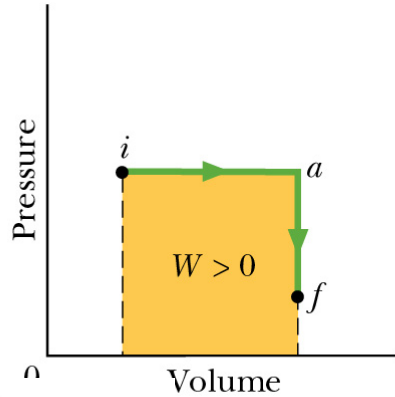=> Non-zero work *needs* a volume change!

There are many different ways to take a system from initial state *i* to the same final state *f*. Work W is the area under the curve on a p-V graph.
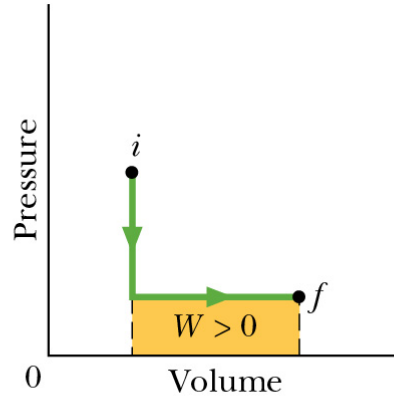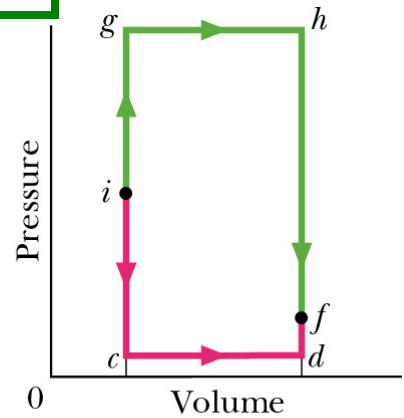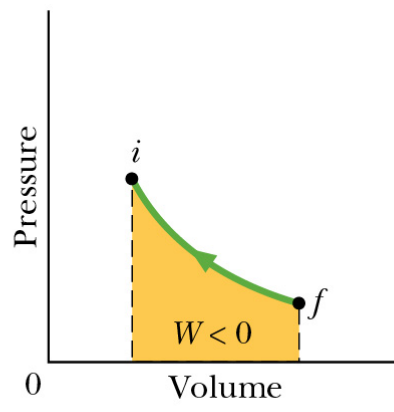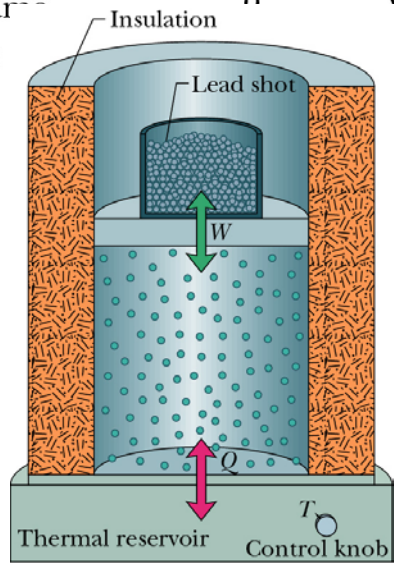
$$W = \int dW = \int_{V_i}^{V_f} p\, dV$$
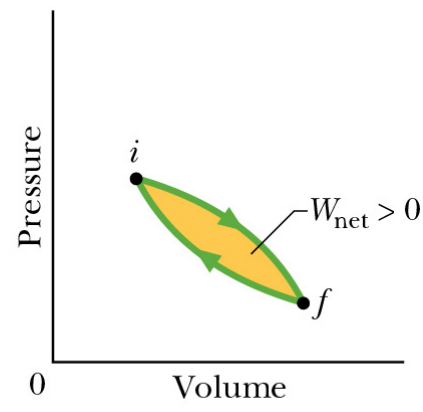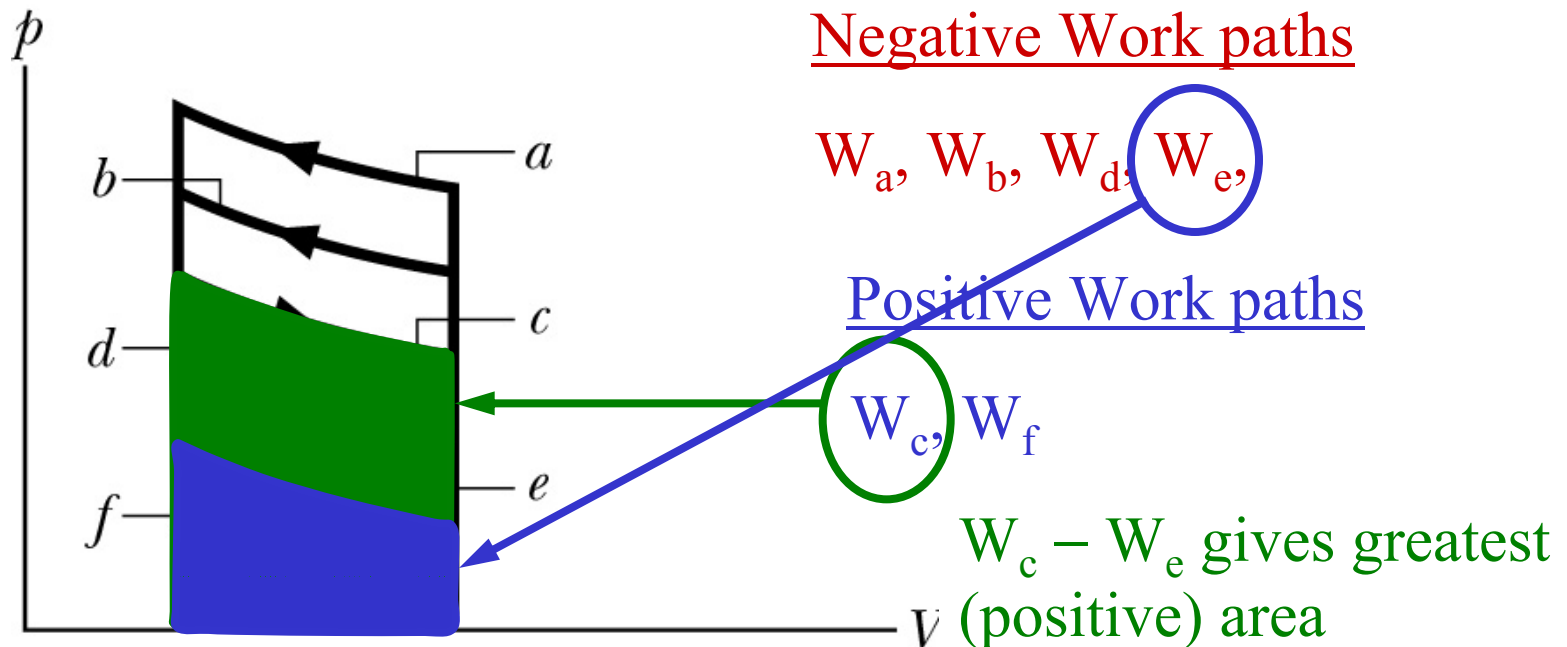
In general, work W and heat Q will have different values for different processes (paths).

Checkpoint: The p-V diagram here shows six curved paths (connected by vertical paths) that can be followed by a gas. Which two of them should be part of a closed cycle if the net work done by the gas is to be at its maximum positive value?

Negative Work paths

W_a, W_b, W_d, W_e,

Positive Work paths

W_c, W_f

$W_c - W_e$ gives greatest (positive) area

The First Law of Thermodynamics

Heat Q and Work W are process (or path)-dependent.

However, **($Q - W$) is independent of the process**. It depends only on the initial and final states and equal to the change in internal energy E_{int}

$$\Delta E_{int} = E_{int\,,f} - E_{int\,,i} = Q - W \qquad \text{(first law)}$$

Think of how much gas it takes to go from here to Bowling Green if you go on I-75 or if you go to Cleveland, then south on I-71, then west on US-6 to BG. Either way, you still start at UT and end up at BG.

The First Law of Thermodynamics

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$$\Delta E_{int} = E_{int,f} - E_{int,i} = Q - W \quad \text{(first law)}$$

Q: "+" heat into the system; "−" heat lost from the system

W: "+" work done by the system. "−" work done on the system

First law of thermodynamics is an extension of the principle of energy conservation to systems that are not isolated.

Problem

The figure here shows four paths on a p-V diagram which a gas can be taken from state i to state f. Rank the paths according to the following parameters, greatest first.

A) the change ΔE_{int}

All paths start at i and end at f, therefore all paths have the same change in internal energy, ΔE_{int}
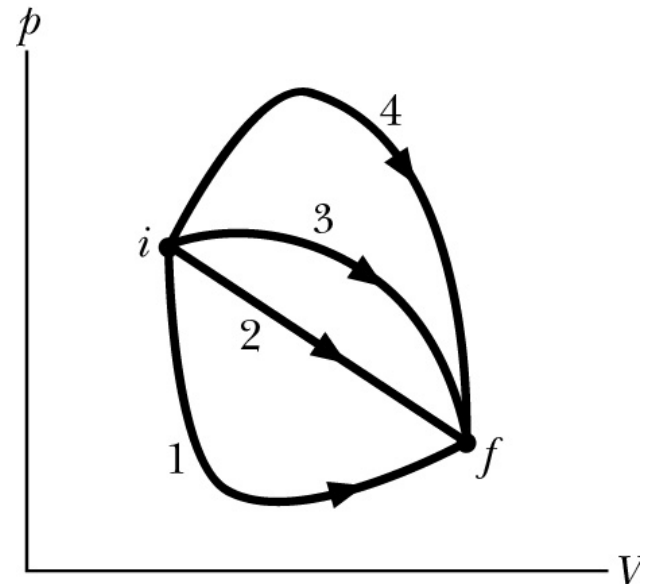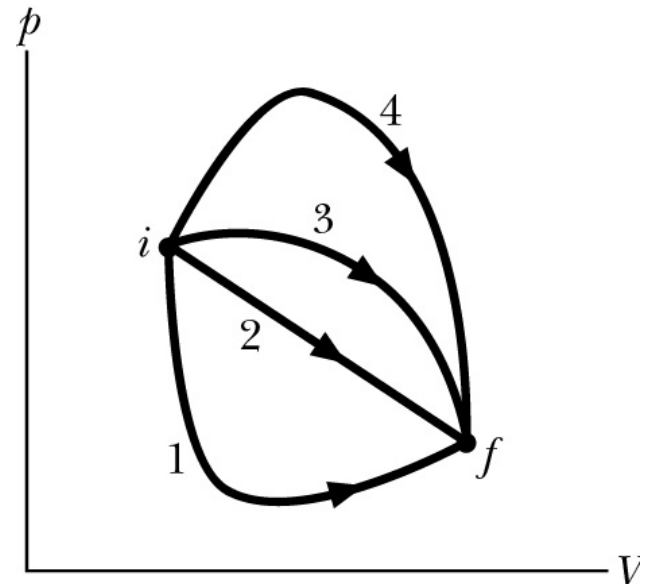
Problem

The figure here shows four paths on a *p-V* diagram which a gas can be taken from state *i* to state *f*. Rank the paths according to the following parameters, greatest first.

B) the greatest work *W* done by the gas

$$W = \int dW = \int_{V_i}^{V_f} p \, dV$$

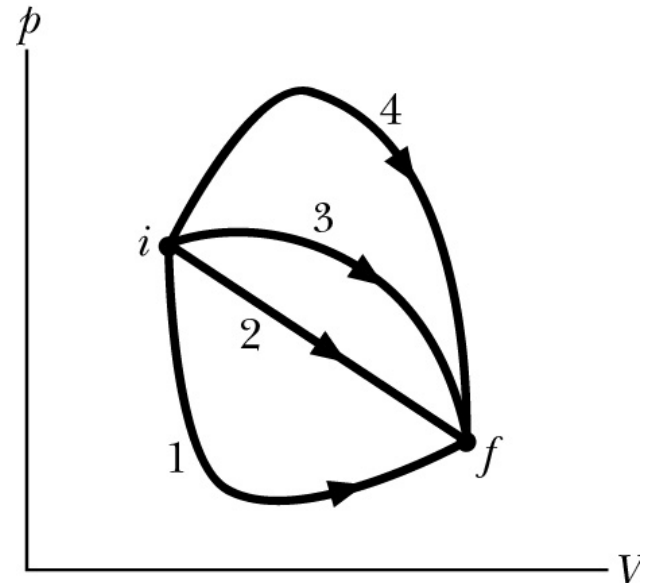Path 4 has the maximum area under the p-V curve.

Problem

The figure here shows four paths on a *p-V* diagram which a gas can be taken from state *i* to state *f*. Rank the paths according to the following parameters, greatest first.

C) the magnitude of the energy transferred as heat Q.

$$\Delta E_{int} = Q - W$$

$$\Rightarrow Q = \Delta E_{int} + W$$

Problem

The figure here shows four paths on a *p-V* diagram which a gas can be taken from state *i* to state *f*. Rank the paths according to the following parameters, greatest first.
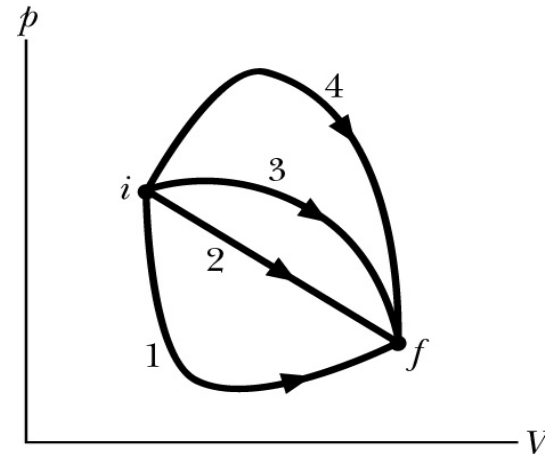
A) the change ΔE_{int}

All paths start at i and end at f, therefore all paths have the same change in internal energy, ΔE_{int}

B) the greatest work *W* done by the gas

$$W = \int dW = \int_{V_i}^{V_f} p\, dV$$

Path 4 has the maximum area under the p-V curve.

C) the magnitude of the energy transferred as heat *Q*.

$$Q = \Delta E_{int} + W$$

W is greatest for path 4 => Q_4 is greatest.

Some special cases of the First Law of Thermodynamics

<u>Adiabatic processes</u>: system insulated, no heat transfer

$$Q = 0 \quad \text{therefore} \quad \Delta E_{int} = Q - W = -W$$

<u>Constant-volume process</u>: V is fixed

$$dW = pdV = 0, \ W = 0 \quad \text{therefore} \quad \Delta E_{int} = Q - W = Q$$

<u>Cyclic processes</u>: System goes back to the initial state

$$\Delta E_{int} = 0 \quad \text{therefore} \quad Q = W$$

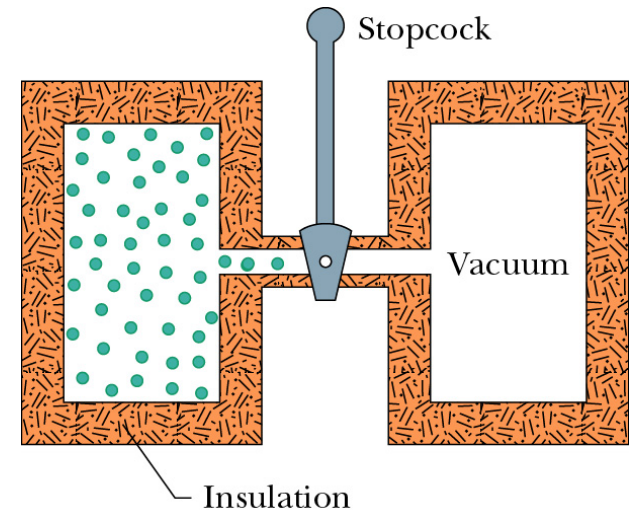# Some special cases of the First Law of Thermodynamics

Free expansion:

insulated => no heat transfer
=> $Q = 0,$
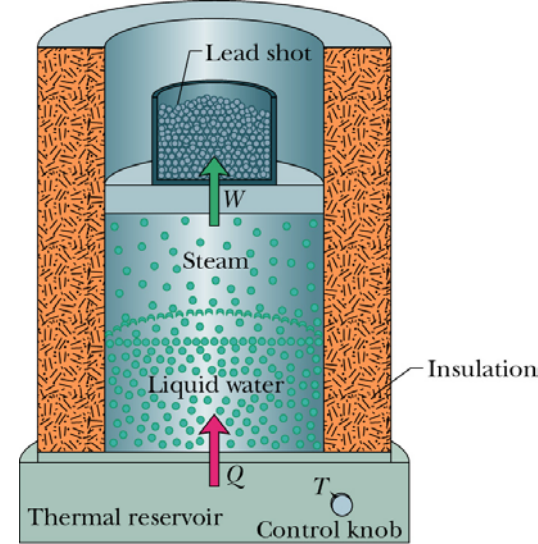

expands into vacuum without pushing something to change its volume
=> $W = 0,$

Therefore: $\Delta E_{int} = Q - W = 0 - 0 = 0$

Let 1.00 kg of liquid water at 100°C be converted to steam at 100°C by boiling at standard atmospheric pressure (1 atm) as shown. The volume of that water changes from an initial value of 1.00 x10⁻³m³ as a liquid to 1.671 m³ as steam.

A) How much work is done by the system during this process?

$$W = \int dW = \int_{V_i}^{V_f} p\, dV = (1.01 \times 10^5)(1.671 - 0.001)J = 169.0 \text{ kJ}$$

B) How much energy is transferred as heat during the process?

$$Q = m\, L_V = (1.00)(2256) = 2256 \text{ kJ}$$

C) What is the change in the system's internal energy during the process?

$$\Delta E_{int} = Q - W = 2256 \text{ kJ} - 169 \text{ kJ} = 2087 \text{ kJ}$$

Heat Transfer Mechanisms

There are three heat transfer mechanisms:

**Conduction**: heat transfer through direct contact.

Convection: Convection happens when a fluid comes in contact with an object whose temperature is higher than that of the fluid. Heat is transferred through the flow of the fluid.

Radiation: Heat can be exchanged via electromagnetic waves, called thermal radiation. It does not need a medium.

Heat Transfer Mechanism

- There are three heat transfer mechanisms: conduction, convection, and radiation

- **Conduction**: heat transfer through direct contact.

$$Q = kA \frac{T_H - T_L}{L} t$$
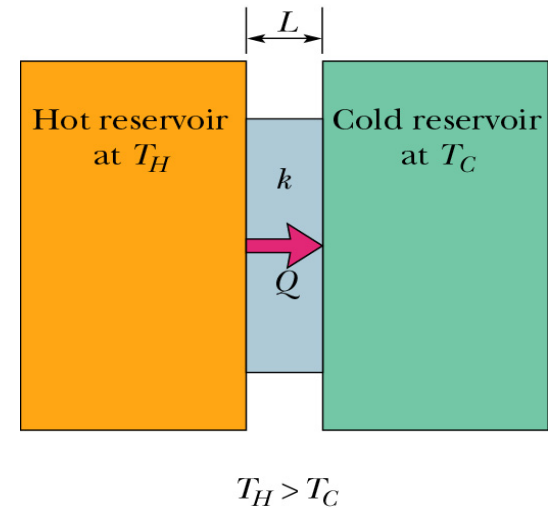
k: thermal conductivity, different for different material. The higher the k value, the better a thermal conductor it is.

e.g. Al: $k = 235$; window glass: $k = 1$ (unit: W/m.K)

- **Conduction rate**: $P_{\text{cond}} = Q/t = kA \, (T_H - T_L) \, /L$

- **Thermal resistance** of a slab of thickness L:

$$R = L / k$$

The higher the R-value, the better a thermal insulator it is.

e.g. R-13 fiberglass insulation for the house: $R = 13 \ ft^2.F^o.h/Btu$

How much heat is lost through $1 \ ft^2$ of this fiberglass in 24 hr period when $T_{outside} = 32^oF$ and $T_{inside} = 72^oF$?

Between R-11 and R-13 fiberglass material for insulation, which one will you pick for your house?

- **Conduction through a composite slab**:

The energy transferred through one material in a certain time must be equal to that transferred through the other material in the same time. i.e. $P_{1,cond} = P_{2,cond}$
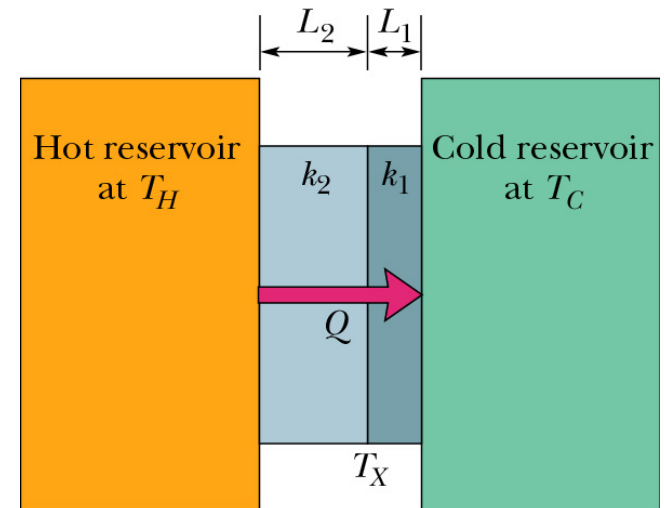
$$P_{cond} = \frac{k_2 A(T_H - T_X)}{L_2} = \frac{k_1 A(T_X - T_C)}{L_1}$$

solve for T_X then

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

For n layers:

$$P_{cond} = \frac{A(T_H - T_C)}{\displaystyle\sum_{i=1}^{n}(L_i / K_i)}$$

examples: "dry wall + insulation +outside wall" for your house, and "shirt + sweater + coat" for your body in the winter.