Thermodynamics

Thermodynamics is the study of the collective properties of a system containing many bodies (typically of order $10^{23}$ !)
Chapter 18 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 familiar with it.

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

room temperature: 290 K
water freezes: 273 K
absolute zero: 0 K
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 $T_3 = 273.16 \text{ K}$

1 Kelvin = $1/273.16$ of the difference between the absolute zero and the triple-point temperature of water.
Triple point of water: water, ice and water vapor coexist in thermal equilibrium. It always occurs at a fixed temperature, $T_3 = 273.16 \text{ K}$.
The constant volume gas thermometer

When $T$ increases, if $V$ is kept constant, $p$ increases

define $T = C \frac{p}{p_0}$ (C is a constant) $\quad p = p_0 - \rho gh$

Now, use it to measure a triple point cell:

$$T_3 = C \frac{p_3}{p_3} \quad \text{so} \quad \frac{T}{T_3} = \frac{p}{p_3}$$

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

At low pressure limit, $T$ measured does not depend on the type of gas

All other thermometers can be calibrated against such measurement
The Celsius and Fahrenheit scales

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

\[ T_C = (T_K - 273.15)°C \]

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

\[ T_F = ((9/5) T_C + 32)°F \]

**Boiling point of water:**

\[ T_C = 100°C, \ T_F = 212°F \]

\[ T_K = 373.15 \text{ K} \]
Thermal Expansion

Most objects expand when they are heated to a higher temperature

**Linear expansion**

\[ \Delta L = \alpha L \Delta T \]

\( \alpha \): coefficient of linear expansion,

\( \alpha = (\Delta L/L)/\Delta T \) unit: 1/K, 1/°C

\( \alpha \) is different for different materials

Al: 2.3x10^{-5}/°C, steel: 1.1x10^{-5}/°C, 1 m long steel ruler, heated up 5°C, \( \Delta L = (1.1 \times 10^{-5}/°C)(1 m)(5°C) = 5.5 \times 10^{-5} m \)
Checkpoint

What happened to the diameter of the **hole** in the ruler when it was heated?

1. It decreased
2. It remained constant
3. It increased according to coefficient of steel
4. It increased according to coefficient of air
5. none of the above
Thermal Expansion

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**Linear expansion**

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\( \alpha \) : coefficient of linear expansion,
\( \alpha = (\Delta L/L)/\Delta T \) unit: 1/K, 1/°C
\( \alpha \) is different for different materials

When a material expands, the spacing between atoms (or molecules) increases → hole diameter increases according to the coefficient of expansion of the material (i.e., steel)
Volume expansion

\[ \Delta V = V \beta \Delta T \]

\( \beta \): coefficient of volume expansion

\[ \beta = 3\alpha \]

A special case: volume expansion of water:

Why do lakes freeze from the top down rather than from the bottom up?
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, $Q = 0$
• **Heat** is **not an intrinsic** property of a system, but a physical property associated with a **process**. **Work** is also associated with a **process**.

• Unit of heat:
  
  – calorie (cal): heat needed to raise the temperature of 1 g of water for 1°C (from 14.5°C to 15.5°C)
  
  – British thermal unit (BTU): heat needed to raise 1 lb water by 1°F (from 63°F to 64°F)
  
  – 1 cal = 3.969 x10⁻³ Btu = 4.1860 J
  
  – “Calorie” in food labels: 1 Calorie (Cal) = 1000 calorie
Microscopic View of Material

How do we know matter is made of atoms?
Absorption of heat by solids and liquids

We’re interested in how well material can absorb energy as we increase its temperature. That quantity is called heat capacity. Heat is absorbed when the temperature of an object is raised from $T_i$ to $T_f$.

\[ Q = C \left( T_f - T_i \right) \]

Units of C: energy/degree, e.g. J/K, cal/°C

The constant $C$ is called the heat capacity of the object. Classical theory predicts this to be a constant $C_V/R = 1/2$ times the number of degrees of freedom.

See Section 19-9, pages 523-525.
Specific heat

• **Specific heat:**
  - It takes more heat to raise same $\Delta T$ 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 material
    - e.g., 1 cal is the heat to raise 1 $^\circ$C for 1 g water:
      \[
      c_{\text{water}} = \frac{Q}{m(T_f - T_i)} = 1 \text{ cal}/(1 \text{ g} \cdot 1^\circ\text{C}) = 4190 \text{ J}/(\text{kg} \cdot \text{K})
      \]
      \[
      c_{\text{Tungsten}} = 134 \text{ J}/(\text{kg} \cdot \text{K}) \ ; \ c_{\text{Al}} = 900 \text{ J}/(\text{kg} \cdot \text{K})
      \]
  - Specific heat is heat capacity per unit mass
    \[ C = m \ c \]
• **Molar specific heat**: heat capacity of 1 mol of substance.

\[ 1 \text{ mol} = 6.02 \times 10^{23} \text{ elementary units} \]

e.g. 1 mol of Al means \(6.02 \times 10^{23}\) Al atoms

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

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

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

since $m_A = m_B$ and $\Delta T_B > \Delta T_A$ $\Rightarrow$ $c_A > c_B$
Toledo vs Minneapolis

In the Spring, many times the winds here in Toledo blow from east to west across Lake Erie whereas in Minneapolis the winds blow across land.

Water has a higher heat capacity than land, therefore it takes more energy *(heat)* to raise its (Lake Erie’s) temperature than land. This energy comes from the winds blowing across Lake Erie, thus cooling the air.

Toledo is *cooler* on those days than Minneapolis even though Minneapolis is much further north than Toledo!
**Heat of Transformation**: When ice melts or water boils, heat is absorbed, but T does not change. The system undergoes a phase transition.

\[ Q = m \, L \]

\( m = \text{mass}, \, L = \text{Latent heat of transformation}. \)

**Heat of vaporization** \( L_V \): For liquid vaporizing to gas, or gas condenses to liquid.

For water, \( L_V = 539 \text{ cal/g} = 2256 \text{ kJ/kg} \)

**Heat of fusion** \( L_F \): For solid melting to liquid, or liquid freezing to solid.

For water, \( L_F = 79.5 \text{ cal/g} = 333 \text{ kJ/kg} \)
1.0 kg of ice at 0°C is converted to steam of 100°C. How much heat is needed?

For water: \( c_w = 1,000 \text{ cal/kg} \cdot ^\circ\text{C} \)

\( L_F = 79,500 \text{ cal/kg} \)
\( L_V = 540,000 \text{ cal/kg} \)

First: Change ice into liquid water at 0°C

\[ Q_F = m L_F = (1.0\text{kg})(79500 \text{ cal/kg}) = 79,500 \text{ cal} \]

Second: Raise the temperature of the water from 0°C to 100°C

\[ Q_w = mc_w \Delta T = (1.0\text{kg})(1000 \text{ cal/kg} \cdot ^\circ\text{C})(100^\circ\text{C}) = 100,000 \text{ cal} \]

Third: Change liquid water into steam at 100°C

\[ Q_V = m L_V = (1.0\text{kg})(540000 \text{ cal/kg}) = 540,000 \text{ cal} \]

Total heat required: \( 79,500 + 100,000 + 540,000 = 719,500 \text{ cal} \)
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 \( V_f \):
\[
W = \int dW = \int_{V_i}^{V_f} p\ dV
\]

\( \Rightarrow \) 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.

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

These areas depend on the path taken to go from $i$ to $f$. 
Checkpoint

Which two paths forming a closed cycle produces the most positive work?

1. path a then e
2. path b then c
3. path e then f
4. path c then e
5. some other path combination
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

Q and W are **process (path)-dependent**.

But,

\[(Q - W) = \Delta E_{\text{int}} \text{ is independent of the process.}\]

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

**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 $f$. Which path has the greatest change in the following parameters?
The figure here shows four paths on a $p-V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

A) the change in internal energy, $\Delta E_{\text{int}}$.

1. 1
2. 2
3. 3
4. 4
5. All paths have the same change
Problem

The figure here shows four paths on a $p-V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

A) the change $\Delta E_{\text{int}}$

All paths start at $i$ and end at $f$, therefore all paths have the same change in internal energy, $\Delta E_{\text{int}}$.
Checkpoint

The figure here shows four paths on a $p$-$V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

B) the greatest work done by the gas, $W$.

1. 1
2. 2
3. 3
4. 4
5. All paths have the same change
Problem

The figure here shows four paths on a $p$-$V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

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.
Checkpoint

The figure here shows four paths on a \( p-V \) diagram which a gas can be taken from state \( i \) to state \( f \). Which path has the greatest change in the following parameters?

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

1. 1
2. 2
3. 3
4. 4
5. All paths have the same change
Problem

The figure here shows four paths on a $p$-$V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

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

\[
\Delta E_{\text{int}} = Q - W
\]

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

$\Delta E_{\text{int}}$ is the same for all four (or for that matter, all) paths between $i$ and $f$.

$\Rightarrow$ path 4 will have the greatest $Q$ transferred
Problem -- Summary

The figure here shows four paths on a $p-V$ diagram which a gas can be taken from state $i$ to state $f$. Which path has the greatest change in the following parameters?

A) the change $\Delta E_{\text{int}}$

All paths start at $i$ and end at $f$, therefore all paths have the same change in internal energy, $\Delta E_{\text{int}}$.

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 $Q$.

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

$W$ is greatest for path 4 $\Rightarrow Q_4$ is greatest because $\Delta E_{\text{int}}$ is the same for all four paths.
Some special cases of the First Law of Thermodynamics

**Adiabatic processes**: system insulated, no heat transfer

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

**Constant-volume process**: V is fixed

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

**Cyclic processes**: System goes back to the initial state

\[ \Delta E_{\text{int}} = 0 \quad \text{therefore} \quad Q = W \]
Some special cases of the First Law of Thermodynamics

**Free expansion:**

- **insulated** $\Rightarrow$ no heat transfer
  $\Rightarrow Q = 0,$

- expands into vacuum without pushing something to change its volume
  $\Rightarrow W = 0,$

Therefore: $\Delta E_{\text{int}} = Q - W = 0 - 0 = 0$
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^-3 m^3 as a liquid to 1.671 m^3 as steam.

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

\[ W = \int dW = \int_{V_i}^{V_f} p\,dV = (1.01\times10^5)(1.671 - 0.001)\,J = 169.0\,kJ \]

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

\[ Q = m\,L_v = (1.00)(2256) = 2256\,kJ \]

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

\[ \Delta E_{\text{int}} = Q - W = 2256\,kJ - 169\,kJ = 2087\,kJ \]
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.
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.
- \( A \): cross-sectional area, \( t \): time

e.g. Aluminum: \( k = 235 \); window glass: \( k = 1 \) (unit: \( \text{W/m} \cdot \text{K} \))

Conduction rate: \( P_{\text{cond}} = \frac{Q}{t} = kA \frac{(T_H - T_L)}{L} /L \)
**Thermal resistance** of a slab of thickness L:

\[ R = \frac{L}{k} \]

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

e.g. R-13 fiberglass insulation for the house: \( R = 13 \, \text{ft}^2 \, \text{oF} \cdot \text{h/Btu} \)

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

\[
Q = kA \left( \frac{T_H - T_L}{L} \right)t = A \left( \frac{T_H - T_L}{R} \right)t
\]

\[
= (1 \, \text{ft}^2) \left( \frac{72 \, \text{oF} - 32 \, \text{oF}}{13 \, \text{ft}^2 \, \text{oF} \cdot \text{h/Btu}} \right)(24\, \text{h}) = 73.8 \, \text{Btu}
\]

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. \( P_{1,\text{cond}} = P_{2,\text{cond}} \)

\[
P_{\text{cond}} = \frac{k_2 A (T_H - T_X)}{L_2} = \frac{k_1 A (T_X - T_C)}{L_1}
\]

solve for \( T_X \):

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

For n layers:

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

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

Think of warm air rising from a heat register
**Radiation**: Heat can be exchanged via electromagnetic waves, called **thermal radiation**. It does not need a medium.

\[ P_{\text{rad}} = \sigma \varepsilon A T^4 \]

\( \sigma = 5.6703 \times 10^{-8} \text{ W/m}^2\cdot\text{K}^4 \) (Stefan-Boltzmann constant)

\( \varepsilon \): emissivity, a value between 0 and 1

A: surface area

T: temperature of the surface in Kelvin

(Classical Approximation -- corrected by Quantum Mechanics)
Problem 18-23

Diets (& fads.......)
Drink plenty of ice water so that the body must expend energy to raise the temperature of ice water up to body temperature.

How many liters of ice water need to be drunk in order for the body to expend the energy equivalent of one lb (0.454 kg) of fat? This much fat requires 3500 Cal to be transferred to the ice water. The water starts at 0°C and body temperature is 37°C.

24. We use \( Q = cm\Delta T \). The textbook notes that a nutritionist’s “Calorie” is equivalent to 1000 cal. The mass \( m \) of the water that must be consumed is

\[
m = \frac{Q}{c\Delta T} = \frac{3500 \times 10^3 \text{ cal}}{(1 \text{ g/cal} \cdot \text{C}^\circ)(37.0^\circ\text{C} - 0.0^\circ\text{C})} = 94.6 \times 10^4 \text{ g},
\]

which is equivalent to \( 9.46 \times 10^4 \text{ g}/(1000 \text{ g/liter}) = 94.6 \) liters of water. This is certainly too much to drink in a single day!
Problem 18-32

Samples A and B are at different initial temperatures when they are placed together.

\( m_A = 5.0 \text{ kg}, \ m_B = 1.5 \text{ kg} \).

Find the specific heat of sample A.

\[
\frac{\Delta y}{\Delta x} = \frac{(4 - 0) ^\circ \text{C}}{(16 - 0) \text{ kJ/kg}} = \frac{1 ^\circ \text{C}}{4 \text{ kJ/kg}} = \frac{1}{c_B}
\]

\[\Rightarrow \ c_B = 4.0 \text{ kJ/kg} ^ \circ \text{C} = 4000 \text{ J/kg} ^ \circ \text{C}\]
Problem 18-32

Samples A and B are at different initial temperatures when they are placed together. 
\[ m_A = 5.0 \text{kg}, \quad m_B = 1.5 \text{ kg}. \]

Find the specific heat of sample A.

34. We note that the heat capacity of sample B is given by the reciprocal of the slope of the line in Figure 18-32(b) (compare with Eq. 18-14). Since the reciprocal of that slope is \( 16/4 = 4 \text{ kJ/kg} \cdot \text{C}^\circ \), then \( c_B = 4000 \text{ J/kg} \cdot \text{C}^\circ = 4000 \text{ J/kg} \cdot \text{K} \) (since a change in Celsius is equivalent to a change in Kelvins). Now, following the same procedure as shown in Sample Problem 18-4, we find

\[
c_A \ m_A \ (T_f - T_A) \ + \ c_B \ m_B \ (T_f - T_B) = 0
\]

\[
c_A \ (5.0 \text{ kg})(40^\circ \text{C} - 100^\circ \text{C}) + (4000 \text{ J/kg} \cdot \text{C}^\circ)(1.5 \text{ kg})(40^\circ \text{C} - 20^\circ \text{C}) = 0
\]

which leads to \( c_A = 4.0 \times 10^2 \text{ J/kg} \cdot \text{K} \).
Problem 18-78

Calculate the heat loss rate for a skier if \( A = 1.8 \text{m}^2 \), clothing thickness \( L = 0.01 \text{m} \), skin temperature = 33\(^\circ\)C, outside temperature = 1\(^\circ\)C

A) thermal conductivity of dry clothing = 0.040 W/m\( \cdot \)K

(a) The rate of heat flow is

\[
P_{\text{cond}} = \frac{kA(T_H - T_C)}{L} = \frac{(0.040 \text{ W/m} \cdot \text{K})(1.8 \text{m}^2)(33^\circ \text{C} - 1.0^\circ \text{C})}{1.0 \times 10^{-2} \text{ m}} = 2.3 \times 10^2 \text{ J/s}.
\]
Problem 18-78

Calculate the heat loss rate for a skier if $A = 1.8 \text{m}^2$, clothing thickness $L = 0.01 \text{m}$, skin temperature $= 33^\circ \text{C}$, outside temperature $= 1^\circ \text{C}$

B) thermal conductivity of wet clothing $= 0.60 \text{ W/m} \cdot \text{K}$

(b) The new rate of heat flow is

$$P'_{\text{cond}} = \frac{k'P_{\text{cond}}}{k} = \frac{(0.60 \text{ W/m} \cdot \text{K})(230 \text{ J/s})}{0.040 \text{ W/m} \cdot \text{K}} = 3.5 \times 10^3 \text{ J/s},$$

which is about 15 times as fast as the original heat flow.