Ground Rules

- Switch off your handphone and pager
- Switch off your laptop computer and keep it
- No talking while lecture is going on
- No gossiping while the lecture is going on
- Raise your hand if you have question to ask
- Be on time for lecture
- Be on time to come back from the recess break to continue the lecture
- Bring your lecture notes to lecture

Thermodynamics – Historical Background

- Thermodynamics and mechanics were considered to be separate branches
  - Until about 1850
  - Experiments by James Joule and others showed a connection between them

- A connection was found between the transfer of energy by heat in thermal processes and the transfer of energy by work in mechanical processes. Since then, the concept of energy was generalized to include internal energy, and after that the Law of Conservation of Energy emerged as a universal law of nature

Internal Energy

- *Internal energy* is all the energy of a system that is associated with its microscopic components
  - These components are its atoms and molecules
  - The system is viewed from a reference frame at rest with respect to the center of mass of the system
Internal Energy and Other Energies

- Internal energy of atoms and molecules also include kinetic energies due to:
  - Random translational motion
  - Rotational motion
  - Vibrational motion
- Internal energy also includes potential energy between molecules

Heat

- Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings, i.e., there will be no heat transfer if the temperatures of system and surroundings are the same.
- The term heat will also be used to represent the amount of energy transferred by this method (difference in temperatures)

Changing Internal Energy

- Both heat and work can change the internal energy of a system
- The internal energy can be changed even when no energy is transferred by heat, but just by work
  - Example, compressing gas with a piston, where energy is transferred by work

Units of Heat

- Historically, the calorie was the unit used for heat
  - One calorie is the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C
    - The “Calorie” (all you hear from TV advertisements) used for food is actually 1 kilocalorie
  - In the US Customary system, the unit is a BTU (British Thermal Unit)
    - One BTU is the amount of energy transfer necessary to raise the temperature of 1 lb of water from 63°F to 64°F
  - The standard used in the textbook by Serway is Joules
Mechanical Equivalent of Heat

- Joule (James Prescott Joule, British Physicist, 1818 - 1889) established the equivalence between mechanical energy and internal energy.
- His experimental setup is shown at right.
- The loss in potential energy associated with the blocks equals the work done by the paddle wheel on the water.
- Temperature of liquid in the container goes up when mechanical work is done.

Mechanical Equivalent of Heat, cont

- Joule found that it took approximately 4.18 J of mechanical energy to raise 1g of water by 1°C.
- Later, more precise measurements determined the amount of mechanical energy needed to raise the temperature of water from 14.5°C to 15.5°C (definition of 1 calorie.)
- 1 cal = 4.186 J
  - This is known as the mechanical equivalent of heat.

Heat Capacity

- The heat capacity, \( C \), of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by 1°C. This means that different mass will have different heat capacity even if they are the same type of matter sample.
- If energy \( Q \) produces a change of temperature of \( \Delta T \), then \( Q = C \Delta T \).

Specific Heat

- Specific heat, \( c \), is the heat capacity per unit mass.
- If energy \( Q \) transfers to a sample of a substance of mass \( m \) and the temperature changes by \( \Delta T \), then the specific heat is \( c = \frac{Q}{m \Delta T} \).
- Specific heat does not vary much especially in a small range of temperature interval.
Specific Heat, cont

- The specific heat is essentially a measure of how insensitive a substance is to the addition of energy.
- The greater the substance’s specific heat, the more energy that must be added to cause a particular temperature change.
- The equation is often written in terms of $Q$:

$$ Q = m \cdot c \cdot \Delta T $$

### Some Specific Heat Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific heat $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J/kg·°C</td>
</tr>
<tr>
<td>Elemental solids</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>900</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1890</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2390</td>
</tr>
<tr>
<td>Copper</td>
<td>387</td>
</tr>
<tr>
<td>Germanium</td>
<td>322</td>
</tr>
<tr>
<td>Gold</td>
<td>129</td>
</tr>
<tr>
<td>Iron</td>
<td>418</td>
</tr>
<tr>
<td>Lead</td>
<td>128</td>
</tr>
<tr>
<td>Silicon</td>
<td>203</td>
</tr>
<tr>
<td>Silver</td>
<td>234</td>
</tr>
</tbody>
</table>

**Example.** Same mass of aluminum and silver are placed in fire and both metals are burned from 24 °C to 200 °C. When the fire is turned off, which metal should you not touch?

**Answer:** Both burns will be bad but the burn from the touch on the aluminum will be more severe than that from the silver.

### More Specific Heat Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific heat $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J/kg·°C</td>
</tr>
<tr>
<td>Other solids</td>
<td></td>
</tr>
<tr>
<td>Brass</td>
<td>380</td>
</tr>
<tr>
<td>Glass</td>
<td>837</td>
</tr>
<tr>
<td>Ice (-5°C)</td>
<td>2960</td>
</tr>
<tr>
<td>Marble</td>
<td>860</td>
</tr>
<tr>
<td>Wood</td>
<td>1700</td>
</tr>
<tr>
<td>Liquids</td>
<td></td>
</tr>
<tr>
<td>Alcohol (ethyl)</td>
<td>2400</td>
</tr>
<tr>
<td>Mercury</td>
<td>140</td>
</tr>
<tr>
<td>Water (15°C)</td>
<td>4186</td>
</tr>
<tr>
<td>Gas</td>
<td></td>
</tr>
<tr>
<td>Steam (100°C)</td>
<td>2010</td>
</tr>
</tbody>
</table>

### Sign Conventions

- **If the temperature of system increases:**
  - $Q$ and $\Delta T$ are positive
  - Energy transfers into the system
- **If the temperature of system decreases:**
  - $Q$ and $\Delta T$ are negative
  - Energy transfers out of the system
Example. The specific heat of concrete is greater than that of soil. A baseball field (with real soil) and the surrounding parking lot (made of concrete) are warmed up during a sunny day. Which would you expect to cool off faster in the evening when the sun goes down?

Answer:

The baseball field, with the lower specific heat, will change temperature more readily, so it will cool off faster. The high specific heat of concrete in parking lot allows it to “retain heat” better and so it will not cool off so quickly—it has a higher “thermal inertia.”

Specific Heat Varies With Temperature

- Technically, the specific heat varies with temperature
- The corrected equation is \( Q = m \int_{T_i}^{T_f} c \, dT \)
- However, if the temperature intervals are not too large, the variation can be ignored and \( c \) can be treated as a constant
  - In general, there is only about 1% variation between 0°C and 100°C for specific heat

Specific Heat of Water

- Water has the highest specific heat of common materials
- This is responsible for many weather phenomena.
  - Global wind systems
  - Land and sea breezes
  - Moderate temperatures near large bodies of water (How?)

Effect of High Specific Heat of Water

The high specific heat of water is responsible, in part, for the moderate temperatures found near large bodies of water. As the temperature of a body of water decreases during the winter, energy is transferred from the cooling water to the air by heat, increasing the internal energy of the air.

Because of the high specific heat of water, a relatively large amount of energy is transferred to the air for even modest temperature changes of the water. The air carries this internal energy landward when prevailing winds are favourable making the coastal area much warmer.
Calorimetry

**Calorimetry** is a technique for measuring specific heat involves heating a material, adding it to a sample of water, and recording the final temperature.

- A calorimeter is a device in which this energy transfer takes place.

Calorimetry, cont

- The system of the sample and the water are treated as two isolated objects.
- Conservation of energy requires that the amount of energy that leaves the sample equals the amount of energy that enters the water.
- Conservation of Energy gives a mathematical expression of this:

$$Q_{\text{cold}} = Q_{\text{hot}}$$

Calorimetry, final

- Let $T_w$ be the initial temperature of water, $T_s$ be the initial temperature of sample, and $T_f$ be the final equilibrium temperature. As heat gained by water is equal to the heat lost by sample, we have

$$m_w c_w (T_f - T_w) = m_s c_s (T_s - T_f)$$

Sample can be found by:

$$c_s = \frac{m_w c_w (T_f - T_w)}{m_s (T_s - T_f)}$$

- Technically, the mass of the container should be included, but if $m_w >> m_{\text{container}}$ it can be neglected.

Example. An 0.0500 kg ingot of metal is heated to 200.0 °C and then dropped into a beaker containing 0.400 kg of water initially at 20.0 °C. If the final equilibrium temperature of the mixed system is 22.4 °C, find the specific heat of the metal.

Answer:

$$c_s = \frac{m_w c_w (T_f - T_w)}{m_s (T_s - T_f)}$$

$$= \frac{(0.400 \text{ kg})(4186 \text{ J/kg} \cdot \text{°C})(22.4 \text{ °C} - 20.0 \text{ °C})}{(0.0500 \text{ kg})(200.0 \text{ °C} - 22.4 \text{ °C})}$$

$$= 453 \text{ J/kg} \cdot \text{°C}$$
Phase Changes

The ice cubes in your coca-cola drink melt. Steam comes out from the coffee in your cup. These are phase changes of water you observe every day.

- A phase change occurs when a substance changes from one form to another
- Two common phase changes are
  - Solid to liquid (melting) -- (opposite: freezing)
  - Liquid to gas (boiling) -- (opposite: condensation)

During a phase change, there is no change in temperature of the substance (e.g., ice melts in water and become ice water. The temperature of ice water (with ice) is also 0 °C – same as the temperature of ice.) (Similarly, boiling water and the steams both remain at 100 °C)

Latent Heat

- The amount of latent energy to change the state of an sample depends on the mass of the sample and its inherent property.
- If an amount of energy $Q$ is required to change the phase of a sample of mass $m$, the latent heat ($L$) of the sample is $L = Q/m$
  - Latent means “hidden”
  - The value of $L$ depends on the substance as well as the actual phase change
  - The energy required to change the phase is $Q = \pm mL$

Sample Latent Heat Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point (°C)</th>
<th>Latent Heat of Fusion (J/kg)</th>
<th>Boiling Point (°C)</th>
<th>Latent Heat of Vaporization (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>-259.65</td>
<td>5.25 \times 10^3</td>
<td>-268.95</td>
<td>2.09 \times 10^3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-209.97</td>
<td>2.55 \times 10^4</td>
<td>-195.81</td>
<td>2.01 \times 10^2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-218.79</td>
<td>1.38 \times 10^5</td>
<td>-182.97</td>
<td>2.13 \times 10^2</td>
</tr>
<tr>
<td>Ethanol alcohol</td>
<td>-114</td>
<td>1.94 \times 10^5</td>
<td>78</td>
<td>8.54 \times 10^2</td>
</tr>
<tr>
<td>Water</td>
<td>0.00</td>
<td>5.33 \times 10^5</td>
<td>100.00</td>
<td>2.26 \times 10^5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>119</td>
<td>3.84 \times 10^3</td>
<td>444.00</td>
<td>8.26 \times 10^3</td>
</tr>
<tr>
<td>Lead</td>
<td>327.5</td>
<td>2.45 \times 10^4</td>
<td>1750</td>
<td>8.70 \times 10^3</td>
</tr>
<tr>
<td>Aluminum</td>
<td>660</td>
<td>3.97 \times 10^5</td>
<td>2450</td>
<td>1.14 \times 10^3</td>
</tr>
<tr>
<td>Silver</td>
<td>960.80</td>
<td>8.82 \times 10^4</td>
<td>2193</td>
<td>2.33 \times 10^5</td>
</tr>
<tr>
<td>Gold</td>
<td>1603.00</td>
<td>6.44 \times 10^5</td>
<td>2660</td>
<td>1.98 \times 10^6</td>
</tr>
<tr>
<td>Copper</td>
<td>1083</td>
<td>1.34 \times 10^5</td>
<td>1187</td>
<td>5.06 \times 10^6</td>
</tr>
</tbody>
</table>
Graph of Ice to Steam
(1 g of ice with initial temperature of -30°C)

Warming Ice, Graph Part A
- Start with one gram of ice at -30.0°C
- During phase A, the temperature of the ice changes from -30.0°C to 0°C
- Use \( Q = m_i c_i \Delta T \)
  - In this case, 62.7 J of energy are added
- \( 0.001 \text{kg} \times 2090 \text{ J/kg°C} \times 30°C \)

Melting Ice, Graph Part B
- Once at 0°C, the phase change (melting) starts
- The temperature stays the same although energy is still being added
- Use \( Q = m_l L_f \)
  - The energy required is 333 J
  - \( 0.001 \text{kg} \times (3.3 \times 10^5) \text{ J/kg} \)
- On the graph, the values move from 62.7 J to 396 J

Warming Water, Graph Part C
- Between 0°C and 100°C, the material is liquid and no phase changes take place
- Energy added increases the temperature
- Use \( Q = m_w c_w \Delta T \)
  - 419 J are added
  - The total is now 815 J
- \( 0.001 \text{kg} \times 4186 \text{ J/kg°C} \times 100°C \)
Boiling Water, Graph Part D

- At 100°C, a phase change occurs (boiling)
- Temperature does not change
- Use \( Q = m_w L_v \)
  - This requires 2260 J
  - The total is now 3075 J

Heating Steam

- After all the water is converted to steam, the steam will heat up
- No phase change occurs
- The added energy goes to increasing the temperature
- Use \( Q = m_s c_s \Delta T \)
  - In this case, 40.2 J are needed
  - The temperature is going to 120°C
  - The total is now 3115 J

Example. In cold regions like Beijing, if you leave equal-size and same-shape open containers of hot water (e.g. 95°C) and colder water (e.g. 70°C) of the same mass outside, which one will freeze first? Why?

Answer:

This happens only when the condition is right. The hot water can freeze faster than the colder water in some cases due to two effects. First, the hot water does actually lose heat faster initially since the temperature difference between the hot water and air is greater than that between the colder water and the air. However the second effect, evaporation is the critical feature. More evaporation will occur from the hot water, reducing the amount of water in the container. With less water to cool, the hot water can actually freeze before the colder water. (Mpemba effect)

Example. Will potatoes cook faster if the water is boiling faster?

Answer:

The water boils at 100°C and remains at that temperature until all of the water has been changed into steam. Only then will the steam increase in temperature. Because the water stays at the same temperature, regardless of how fast it is boiling, the potatoes will not cook any faster.

How can you cook the potatoes faster?
Molecular View of Phase Changes

- Phase changes can be described in terms of the rearrangement of molecules (or atoms in an elemental substance)
- Liquid to Gas phase change
  - Molecules in a liquid are close together
  - The forces between them are stronger than those in a gas
  - Work must be done to separate the molecules
  - The latent heat of vaporization is the energy per unit mass needed to accomplish this separation

Molecular View of Phase Changes, cont

- Solid to Liquid phase change
  - The addition of energy will cause the amplitude of the vibration of the molecules about their equilibrium position to increase
  - At the melting point, the amplitude is great enough to break apart bonds between the molecules
  - The molecules can move to new positions
  - The molecules in the liquid are bound together less strongly than those of the solid
  - The latent heat of fusion is the energy per unit mass required to go from the solid-type to the liquid-type bonds

Molecular View of Phase Changes, final

- The latent heat of vaporization is greater than the latent heat of fusion
  - In the liquid-to-gas phase change, the liquid-type bonds are broken
  - The gas molecules are essentially not bonded to each other
  - It takes more energy to completely break the bonds than to change the type of bonds

Calorimetry Problem-Solving Strategy

- Units of measure must be consistent
  - For example, if your value of $c$ is in J/kg°C, then your mass must be in kg, the temperatures in °C and energies in J
- Transfers of energy are given by $Q = mc \Delta T$
  - only when no phase change occurs
  - If there is a phase change, use $Q = mL$
**Example.** A 3.00-g lead bullet at 30.0°C is fired at a speed of 240 m/s into a large block of ice at 0°C, in which it becomes embedded. What quantity of ice melts?

**Answer:**

The bullet will not melt all the ice, so its final temperature is 0°C.

\[
\left( \frac{1}{2} m v^2 + m c \Delta T \right)_{\text{bullet}} = m_w L_f
\]

\( m_w : \text{the melt water mass} \)

\[
m_w = \frac{0.500 \left( 3.00 \times 10^{-3} \text{ kg} \right) \left( 240 \text{ m/s} \right)^2 + 3.00 \times 10^{-3} \text{ kg} \left( 128 \text{ J/kg°C} \right) \left( 30.0°C \right)}{3.33 \times 10^5 \text{ J/kg}}
\]

\[
m_w = \frac{86.4 \text{ J} + 11.5 \text{ J}}{333 \times 10^3 \text{ J/kg}} = 0.294 \text{ g}
\]

---

**State Variables**

- State variables describe the state of a system. This has nothing to do with phase change.
- In the macroscopic approach to thermodynamics, variables are used to describe the state of the system:
  - Pressure, temperature, volume, internal energy are examples of state variables.
- The macroscopic state of an isolated system can be specified only if the system is in thermal equilibrium internally.

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**Transfer Variables**

- Heat (Q) and work (W) are transfer variables (create the occurrence of events!)
  - Example of heat: we can only assign a value of the heat if energy crosses the boundary by heat (i.e., something has happened – what is the something?)
- Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system.
- Transfer variables are not associated with any given state of the system, only with changes in the state.
Work in Thermodynamics

- Work can be done on a deformable system, such as a gas.
- Consider a cylinder with a moveable piston.
- A force is applied to slowly compress the gas.
  - The compression is slow enough for all the system to remain essentially in thermal equilibrium (i.e., the temperature remains a constant.)
- This is said to occur quasi-statically.

The work done on the gas is:
\[ dW = -P \, dV \]

Interpreting \( dW = -P \, dV \)
- If the gas is compressed, \( dV \) is negative and the work done on the gas is positive.
- If the gas expands, \( dV \) is positive and the work done on the gas is negative.
- If the volume remains constant, the work done is zero.

The total work done is:
\[ W = -\int_{V_i}^{V_f} P \, dV \]

PV Diagrams

- Used when the pressure and volume are known at each step of the process.
- The state of the gas at each step can be plotted on a graph called a PV diagram.
  - This allows us to visualize the process through which the gas is progressing.
- The curve is called the path from initial state to final state.
**PV Diagrams, cont**

- The work done on a gas in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on the PV diagram, evaluated between the initial and final states.
  - This is true whether or not the pressure stays constant.
  - The work done depends on the path taken.

**Heat Transfer, Example 1**

**Example.** A gas at temperature $T_i$ expands slowly while absorbing energy from a reservoir in order to maintain a constant temperature.

- The energy transfer, $Q$, into or out of a system also depends on the process.
- The energy reservoir is a source of energy that is considered to be so great that a finite transfer of energy does not change its temperature.
- The piston is pushed upward, the gas is doing work on the piston.

**Heat Transfer, Example 2**

**Example.** A gas expands rapidly into an evacuated region after a membrane is broken.

- This gas has the same initial volume, temperature and pressure as the previous example.
- The final states are also identical with the final state of previous example.
- No energy is transferred by heat through the insulating wall.
- No work is done by the gas expanding into the vacuum.

**Work Done By Various Paths**

- Each of these processes has the same initial and final states.
- But the work done differs in each process.
- The work done depends on the path of change.
Work From a $P\!V$ Diagram, Example 1

- The volume of the gas is first reduced from $V_i$ to $V_f$ at constant pressure $P_i$.
- Next, the pressure increases from $P_i$ to $P_f$ by heating at constant volume $V_f$.
- $W = -P_i (V_f - V_i)$

Work From a $P\!V$ Diagram, Example 2

- The pressure of the gas is increased from $P_i$ to $P_f$ at a constant volume.
- The volume is decreased from $V_i$ to $V_f$.
- $W = -P_f (V_f - V_i)$

Work From a $P\!V$ Diagram, Example 3

- The pressure and the volume continually change.
- The work is some intermediate values between $-P_f (V_f - V_i)$ and $-P_i (V_f - V_i)$.
- To evaluate the actual amount of work, the function $P(V)$ must be known.

Energy Transfer, Summary

- Energy transfers by heat, like the work done, depends on the initial, final, and intermediate states of the system.
- Both work and heat depend on the path taken, i.e., all the intermediate points must be considered.
- Neither can be determined solely by the end points (i.e., only the start point and the finish point) of a thermodynamic process.
The First Law of Thermodynamics

- The First Law of Thermodynamics is a special case of the Law of Conservation of Energy
  - It takes into account changes in internal energy ($\Delta E_{int}$) and energy transfers by heat (Q) and work (W)
- Although $Q$ and $W$ each are individually dependent on the path, $(Q + W)$ is independent of the path
- The First Law of Thermodynamics states that $\Delta E_{int} = Q + W$
  - All quantities must have the same units of measure of energy

Example. A sample of an ideal gas is in a vertical cylinder fitted with a piston. As 5.79 kJ of energy is transferred to the gas by heat to raise its temperature. The weight on the piston is adjusted so that the state of the gas changes from point A to point B along the semicircle shown in Figure. Find the change in internal energy of the gas.

Answer:
The area of a true semicircle is $\frac{1}{2} \times (\pi \times r_1 \times r_2)$.
The area of semi-circle is:
$$\frac{1}{2} \pi (2A \text{L})(200 \text{kPa}) \approx \frac{1}{2} \pi \left(2 \times 10^{-3} \text{ m}^3\right)(2 \times 10^5 \text{ N/m}^2)$$
The work on the gas is
$$W = -\int_A^B PdV = -\text{area under the arch shown in the graph}$$
$$= -\left(\frac{1}{2} \pi 2A(200) \text{J} + 3 \times 10^5 \text{ N/m}^2 \times 4.8 \times 10^{-3} \text{ m}^3\right)$$
$$= -(754 \text{ J} + 1440 \text{ J}) = -2190 \text{ J}$$
$\Delta E_{int} = Q + W = 5790 \text{ J} - 2190 \text{ J} = 3600 \text{ kJ}$

Isolated Systems

- An isolated system is one that does not interact with its surroundings
  - No energy transfer by heat takes place
  - The work done on the system is zero
  - $Q = W = 0$, so $\Delta E_{int} = 0$
- The internal energy of an isolated system remains constant
Cyclic Processes

- A cyclic process is one that starts and ends in the same state
  - This process would not be isolated
  - On a $PV$ diagram, a cyclic process appears as a closed curve
- The change in internal energy must be zero ($\Delta E_{int} = 0$) since internal energy is a state variable and the start and end points are the same (same state)
- As $\Delta E_{int} = Q + W \rightarrow Q = -W$
- In a cyclic process, the net work done on the system per cycle equals the area enclosed by the path representing the process on a $PV$ diagram

Adiabatic Process

- An adiabatic process is one during which no energy enters or leaves the system by heat
  - $Q = 0$
  - This is achieved by:
    - Thermally insulating the walls of the system
    - Having the process proceed so quickly that no heat can be exchanged within a very short time
  - $\Delta E_{int} = Q + W$

Adiabatic Process, cont

- Since $Q = 0$, $\Delta E_{int} = W$
- If the gas is compressed adiabatically, $W$ is positive so $\Delta E_{int}$ is positive and the temperature of the gas increases
- If the gas expands adiabatically, the temperature of the gas decreases

Adiabatic Free Expansion

- This is an example of adiabatic free expansion
- The process is adiabatic because it takes place in an insulated container
- Because the gas expands into a vacuum, it does not apply a force on a piston and $W = 0$
- Since $Q = 0$ and $W = 0$, $\Delta E_{int} = 0$ so the initial and final energies of the gas are the same
  - No change in temperature is expected
Example. You pump air into a basket ball. The plunger of a pump is pushed down rapidly with the end of the pump sealed so that air does not escape and there is little time for heat to flow through the cylinder wall. Explain why the cylinder of the pump becomes warm.

Answer:
Since the compression occurs rapidly, there is no time for heat to flow into or out of the system. To a very good approximation, the process may be treated as an adiabatic compression, and $Q = 0$. Since work is done on the system, $W$ is positive. Therefore the change in the internal energy, $\Delta E_{int}$, is positive. The work done by the person pushing the plunger is manifested as an increase in the internal energy of the air in the pump. The internal energy of an ideal gas is proportional to the Kelvin temperature. Since the internal energy of the gas increases, the temperature of the air in the pump must also increase. This increase in temperature is evidenced by the fact that the pump becomes warm.

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

Isothermal Process

- An isothermal process is one that occurs at a constant temperature
- Since there is no change in temperature, $\Delta E_{int} = 0$
- Therefore, $Q = -W$
- Any energy that enters the system by heat must leave the system by work
- How this is done? When work is done on/by the gas in volume compression/expansion, it needs an energy reservoir to absorb/supply heat energy from/to the gas to maintain the constant temperature.

Isothermal Process, cont

- At right is a $PV$ diagram of an isothermal expansion
- The curve is a hyperbola
- The curve is called an isotherm

Isothermal Expansion

- The curve of the $PV$ diagram indicates $PV = \text{constant}$
- The curve is a hyperbola
- Because it is an ideal gas and the process is quasi-static, $PV = nRT$ and 
  
  $$W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$
  
  $$W = nRT \ln \left( \frac{V_i}{V_f} \right)$$
Isothermal Expansion

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

- Numerically, the work equals the area under the $PV$ curve.
- The shaded area in the diagram.
- If the gas expands ($V_f > V_i$), the work done on the gas is negative.
- If the gas is compressed ($V_f < V_i$), the work done on the gas is positive.

Ideal Gas Isotherms

If the volume of the ideal gas is increased (the gas is expanded), it requires heat energy to enter the system to remain on the same isotherm.

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Isobaric Processes

- An isobaric process is one that occurs at a constant pressure.
- The values of the heat and the work are generally both nonzero.
- The work done on the gas is $W = -P(V_f - V)$ where $P$ is the constant pressure.
- An isobaric compression can be done by cooling the gas (e.g., with ice) when the gas is being compressed by the piston.

\[ \Delta E_{int} = Q + W \]
Isovolumetric Processes

- An isovolumetric process is one in which there is no change in the volume (`clamp the piston`).
- Since the volume does not change, \( \int W = 0 \).
- From the first law, \( \Delta E_{\text{int}} = Q \).
- If energy is added by heat to a system kept at constant volume, all of the transferred energy remains in the system as an increase in its internal energy.

This is how you can cook your potatoes faster!

An Isothermal Expansion

**Example.** A 1.0 mol of an ideal gas is kept at 0°C during an expansion from 3.0 L to 10.0 L.

(A). Find the work done on the gas during the expansion.

**Answer:**

\[
W = nRT \ln \left( \frac{V_f}{V_i} \right) = (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K}) \ln \left( \frac{10.0 \text{ L}}{3.0 \text{ L}} \right) = -2.7 \times 10^3 \text{ J}
\]

(B). How much energy transfer by heat occurs with the surroundings in this process?

**Answer:**

From the first law: \( \Delta E_{\text{int}} = Q + W \)

An Isobaric Compression

(C). If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas during the compression.

**Answer:**

Work done on the gas in an isobaric process is:

\[
W = -P(V_f - V_i)
\]

where \( V_f = 10.0 \text{ L} \) and \( V_i = 3.0 \text{ L} \)

(reverse of part A)

\[
W = -P(V_f - V_i) = - \left( \frac{nRT}{V_i} \right)(V_f - V_i)
\]

\[
W = -(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K}) \frac{10.0 \times 10^{-3} \text{ m}^3}{(3.0 - 10.0) \times 10^{-3} \text{ m}^3} \Rightarrow
\]

\[
W = 1.6 \times 10^3 \text{ J}
\]

(D). Will the temperature of gas remain as 0°C (i.e., still isothermal) at the end of the isobaric compression in (C)?

**Answer:**

No. The temperature will be lower than 0°C.
\[ \Delta E_{\text{int}} = Q + W \]

Special Processes, Summary

- **Adiabatic**
  - No heat exchanged
  - \( Q = 0 \) and \( \Delta E_{\text{int}} = W \)

- **Isobaric**
  - Constant pressure
  - \( W = -P(V_f - V_i) \) and \( \Delta E_{\text{int}} = Q + W \)

- **Isothermal**
  - Constant temperature
  - \( \Delta E_{\text{int}} = 0 \) and \( Q = -W \)

- **Isovolumetric**
  - Constant volume
  - \( W = 0 \) and \( \Delta E_{\text{int}} = Q \)

---

### Heating a Solid

**Example.** A **1.0 kg** bar of copper is heated at atmospheric pressure. If its temperature increases from **20°C** to **50°C**.

**(A).** Find the work done on the copper bar by the surrounding atmosphere?

**Answer:**

The process is isobaric.

\[
\Delta V = 3aV_i \Delta T = \left( 5.1 \times 10^{-5} \ ^\circ C^{-1} \right) \left( 30 \ ^\circ C \right) V_i = 1.5 \times 10^{-3} V_i
\]

\[
= 1.5 \times 10^{-3} \frac{m}{\rho_{Cu}} = 1.5 \times 10^{-3} \frac{1.0 \ kg}{8.92 \times 10^3 \ kg/m^3} = 1.7 \times 10^{-7} m^3
\]

\[
W = -P_{i} \Delta V = -\left( 1.013 \times 10^5 \ N/m^2 \right) \left( 1.7 \times 10^{-7} m^3 \right) = -1.7 \times 10^{-2} J
\]

Since work is negative, this work is done by the copper bar on the atmosphere.

---

**Heating a Solid, final**

**(B).** How much energy is transferred to the copper bar by heat?

**Answer**

\[
Q = mc\Delta T = (1.0 \ kg)(387 \ J/\ kg \cdot ^\circ C)(30 ^\circ C) = 1.2 \times 10^4 \ J
\]

**(C).** What is the increase in internal energy of the copper bar?

**Answer**

\[
\Delta E_{\text{int}} = Q + W = 1.2 \times 10^4 J + (-1.7 \times 10^{-2} J) = 1.2 \times 10^4 J
\]
**Mechanisms of Heat Transfer**

- We want to know the rate at which energy is transferred
- There are various mechanisms responsible for the transfer:
  - Conduction
  - Convection
  - Radiation

**Conduction**

- The transfer can be viewed on an atomic scale
  - It is an exchange of energy between microscopic particles by collisions
    - The microscopic particles can be atoms, molecules, or free electrons
    - Less energetic particles gain energy during collisions with more energetic particles
  - Rate of conduction depends upon the characteristics of the substance

**Conduction example**

- The molecules vibrate about their equilibrium positions
- Particles (molecules) in the pan near the heat source vibrate with larger amplitudes
- These molecules collide with adjacent molecules and transfer some energy
- Eventually, the energy travels entirely through the pan

**Conduction, cont.**

- In general, metals are good heat conductors
  - They contain large numbers of electrons that are relatively free to move through the metal
  - They can transport energy from one region to another
- Poor heat conductors include asbestos, paper, and gases
- Conduction can occur only if there is a difference in temperature between two parts of the conducting medium
Conduction, equation

- The slab at right allows energy to transfer from the region of higher temperature to the region of lower temperature.
- The rate of transfer is given by:

\[ \dot{Q} = \frac{Q}{\Delta t} = kA \left| \frac{dT}{dx} \right| \]

- \( \dot{Q} \) is the rate of energy transfer.
- \( h \) is in Watts when \( Q \) is in Joules and \( t \) is in seconds.
- \( k \) (Unit is \( \text{W m}^{-1} \text{K}^{-1} \)) is the thermal conductivity of the material.
- Good conductors have high \( k \) values and good insulators have low \( k \) values.

Temperature Gradient

- The quantity \( | \frac{dT}{dx} | \) is called the **temperature gradient** of the material.
- It measures the rate at which temperature varies with position.
- For a rod, the temperature gradient can be expressed as:

\[ \left| \frac{dT}{dx} \right| = \frac{T_h - T_c}{L} \]

Rate of Energy Transfer in a Rod

- Using the temperature gradient for the rod, the rate of energy transfer becomes:

\[ \dot{Q} = kA \left( \frac{T_h - T_c}{L} \right) \]
Compound Slab

- For a compound slab containing several materials of various thicknesses ($L_1, L_2, ...$) and various thermal conductivities ($k_1, k_2, ...$) the rate of energy transfer depends on the materials and the temperatures at the outer edges:

$$
\phi = A \left( T_h - T_c \right) \sum_i \left( \frac{L_i}{k_i} \right)
$$

$$
\frac{Q}{\Delta t} = kA \frac{dT}{ds}
$$

$$
\phi = kA \left( \frac{T_h - T_c}{L} \right)
$$

Some Thermal Conductivities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Thermal Conductivity (W/m °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals (at 25°C)</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>238</td>
</tr>
<tr>
<td>Copper</td>
<td>397</td>
</tr>
<tr>
<td>Gold</td>
<td>314</td>
</tr>
<tr>
<td>Iron</td>
<td>79.5</td>
</tr>
<tr>
<td>Lead</td>
<td>34.7</td>
</tr>
<tr>
<td>Silver</td>
<td>427</td>
</tr>
</tbody>
</table>

More Thermal Conductivities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Thermal Conductivity (W/m °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonmetals</td>
<td></td>
</tr>
<tr>
<td>(approximate values)</td>
<td></td>
</tr>
<tr>
<td>Asbestos</td>
<td>0.08</td>
</tr>
<tr>
<td>Concrete</td>
<td>0.8</td>
</tr>
<tr>
<td>Diamond</td>
<td>2.300</td>
</tr>
<tr>
<td>Glass</td>
<td>0.8</td>
</tr>
<tr>
<td>Ice</td>
<td>2</td>
</tr>
<tr>
<td>Rubber</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>0.6</td>
</tr>
<tr>
<td>Wood</td>
<td>0.08</td>
</tr>
</tbody>
</table>

More Thermal Conductivities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Thermal Conductivity (W/m °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases (at 20°C)</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>0.0234</td>
</tr>
<tr>
<td>Helium</td>
<td>0.138</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.172</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0234</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0238</td>
</tr>
</tbody>
</table>
Example. Fruit growers often spray their crops with water to protect them from freezing in unusually cold weather. How does liquid water keep the fruit from freezing?

**Answer:**

Liquid water releases a large amount of heat (Water: Specific Heat: 4186 J/kg°C, Latent Heat of Fusion = 3.33x10^5 J/kg) as it solidifies and this heat helps to protect the fruit from freezing. As cold air removes heat from the water-coated fruit, the water begins to freeze. The heat released by water prevents the fruit’s temperature from dropping below 0°C until the water has completely turned to ice.

---

**Example.** Two rods from different materials with the same length and diameter are connecting two regions of different temperatures. In which case is the rate of energy transfer by heat larger?

**Answer (qualitative explanation):**

*In parallel.* The rods arranged in parallel present a larger area \( A \) (more contact) and a smaller length \( L \) (shorter distance) through which the energy can transfer.

---

**Example.** A bar of gold is in thermal contact with a bar of silver of the same length and area. One end of the compound bar is maintained at 80.0°C while the opposite end is at 30.0°C. When the energy transfer reaches steady state, what is the temperature at the junction?

**Answer:**

In the steady state condition, \( P_{Au} = P_{Ag} \)

\[
\Delta T = \frac{k_{Au}}{k_{Ag}} \Delta T
\]

In this case (lengths and areas)

\[
\Delta x_{Au} = \Delta x_{Ag}
\]

\[
A_{Au} = A_{Ag}
\]

\[
\Delta T_{Au} = (80 - T)
\]

\[
\Delta T_{Ag} = (T - 30)
\]

\[
k_{Au} (80 - T) = k_{Ag} (T - 30)
\]

\[
T = 51.2°C
\]

\[
314 \text{ W/m°C}
\]

\[
427 \text{ W/m°C}
\]

---

**Home Insulation**

- Substances are rated by their \( R \) values
  - \( R = \frac{L}{k} \) and the rate becomes
    \[
    \varphi = \frac{A(T_h - T_c)}{\sum R_i}
    \]
  - For multiple layers, the total \( R \) value is the sum of the \( R \) values of each layer
  - Wind increases the energy loss by conduction in a home because the \( R \) value of air in the gap of hollow wall is not optimal
Table 20.4

<table>
<thead>
<tr>
<th>Material</th>
<th>R value ($\text{F}^2 \cdot \text{F} \cdot \text{h}/\text{Btu}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood siding (1 in. thick)</td>
<td>0.91</td>
</tr>
<tr>
<td>Wood shingles (lapped)</td>
<td>0.87</td>
</tr>
<tr>
<td>Brick (4 in. thick)</td>
<td>4.00</td>
</tr>
<tr>
<td>Concrete block (filled cores)</td>
<td>1.93</td>
</tr>
<tr>
<td>Fiberglass insulation (3.5 in. thick)</td>
<td>10.90</td>
</tr>
<tr>
<td>Fiberglass insulation (6 in. thick)</td>
<td>18.80</td>
</tr>
<tr>
<td>Fiberglass board (1 in. thick)</td>
<td>4.35</td>
</tr>
<tr>
<td>Cellulose fiber (1 in. thick)</td>
<td>3.70</td>
</tr>
<tr>
<td>Flat glass (0.125 in. thick)</td>
<td>0.89</td>
</tr>
<tr>
<td>Insulating glass (0.25-in. space)</td>
<td>1.54</td>
</tr>
<tr>
<td>Air space (3.5 in. thick)</td>
<td>1.01</td>
</tr>
<tr>
<td>Stagnant air layer</td>
<td>0.17</td>
</tr>
<tr>
<td>Drywall (0.5 in. thick)</td>
<td>0.45</td>
</tr>
<tr>
<td>Sheathing (0.5 in. thick)</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Fiberglass insulation (3.5-inch thickness): **10.90**

Air space (3.5-inch thickness): **1.01**

Material with the higher R value should be used to fill in the gap between the walls. But this can be more costly.

---

**Convection**

- Energy transferred by the movement of a substance
  - When the movement results from differences in density, it is called *natural convection*
  - When the movement is forced by a fan or a pump, or any artificial means, it is called *forced convection*

**Convection example**

- Air directly above the radiator is warmed and expands
- The density of the air decreases, and it rises
- A continuous air current is established
Radiation
- Radiation does not require physical contact.
- All objects radiate energy continuously in the form of electromagnetic waves due to thermal vibrations of their molecules.
- Rate of radiation is given by Stefan’s law.

Stefan’s Law
- \( P = \sigma A e T^4 \)
  - \( P \) is the rate of energy transfer, in Watts.
  - \( \sigma = 5.6696 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4 \) (constant).
  - \( A \) is the surface area of the object.
  - \( e \) is a constant called the emissivity.
    - \( e \) varies from 0 to 1.
    - The emissivity is also equal to the absorptivity.
  - \( T \) is the temperature in Kelvin's and is with respect to 0°C.

Energy Absorption and Emission by Radiation
- With its surroundings, the rate at which the object at temperature \( T \) with surroundings at \( T_0 \) radiates is
  - \( P_{\text{net}} = \sigma A e (T^4 - T_0^4) \)
  - When an object is in equilibrium with its surroundings, it radiates and absorbs at the same rate.
    - Its temperature will not change.

Example. The surface of the Sun has a temperature of about 5800 K. The radius of the Sun is 6.96 \times 10^8 m. Calculate the total energy radiated by the Sun each second. Assume that the emissivity is 0.965.

Answer:

\[
P = \sigma A e T^4
\]

\[
= \left(5.6696 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4\right) \left[4\pi \left(6.96 \times 10^8 \text{ m}\right)^2\right] (0.965)(5800 \text{ K})^4
\]

\[
P = 3.77 \times 10^{26} \text{ W}
\]

This is an abundant amount of energy beyond our imagination.
**Ideal Absorbers**

- An *ideal absorber* is defined as an object that absorbs all of the energy incident on it
  - **emissivity** $e = 1$
- This type of object is called a **black body**
- An ideal absorber is also an ideal radiator of energy

**Ideal Reflector**

- An ideal reflector absorbs none of the energy incident on it
  - $e = 0$

**Example.** Energy from the Sun reaches the Earth at 1000 W/m² on a relatively clear day. If a person lying flat on the beach is exposed to the Sun at 30° angle with the vertical, and the area of body exposed to the Sun is 0.8 m², and the emissivity of exposed body is 0.7, what rate does the body absorb the heat energy from the Sun light?

**Answer:**

The rate of the heat energy absorbed by the person is

$$(1000 \text{ W/m}^2) e A \cos \Theta$$

$$= (1000 \text{ W/m}^2) (0.7 \times 0.8 \text{ m}^2 \times 0.866)$$

$$= 485 \text{ W}$$
The Dewar Flask

- A Dewar flask is a container designed to minimize the energy losses by conduction, convection, and radiation.
- It is used to store either cold or hot liquids for long periods of time.
  - A Thermos bottle is a common household equivalent of a Dewar flask.

Dewar Flask, Details

- The space between the walls is a vacuum to minimize energy transfer by conduction and convection.
- The silvered surface minimizes energy transfers by radiation.
  - Silver is a good reflector.
- The size of the neck is reduced to further minimize energy losses.

You can use any container. But type B will keep your soup hot for a longer time due to its narrow neck that reduces energy loss when the cover is removed. Your customers will be happier when they are served with hot soup than cold soup.