Chapter 18

Heat and the First Law of Thermodynamics

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Brownian Motion

In 1801 Brown, through the influence of Joseph Banks, obtained the post of naturalist on a voyage to Australia, bringing back over 4000 species of plants. In 1827 Brown was viewing a suspension of pollen in water under the microscope and noticed an irregular movement of the grains. He initially thought that the pollen contained some life-form but when he noticed the same effect with dye particles he was at a loss to explain the phenomenon. It was another 50 years before Maxwell and Einstein were to explain the effect. It was the first evidence for atomism that was an observation rather than a deduction.

See videos from YouTube

Thermodynamics – Historical Background

Thermodynamics and mechanics were considered to be separate branches of Physics

- 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

- The concept of energy was generalized to include internal energy
- 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 centre of mass of the system.

\[
U = \text{PE}_g + \text{PE}_{\text{chem}} + E_{\text{mass}} + E_{\text{rot}} + E_{\text{vib}} + \text{KE}_{\text{random}}
\]
Internal Energy & Other Energies

- The kinetic energy due to motion through space is **not** included.
- Internal energy does include kinetic energies due to:
  - Random translational motion
  - Rotational motion
  - Vibrational motion
- Internal energy also includes potential energy between molecules.

TDM03AN2: Thermal Energy

\[ Q = E_{\text{rot}} + E_{\text{vib}} + KE_{\text{random}} \]
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.
- The term *heat* will also be used to represent the *amount* of energy transferred by this method.
Heat does not mean Hot!

- In everyday language we use the word “heat” when describing how hot something is. This is not a scientifically correct usage!
- However we’re stuck with the bad use of language! It is a historical accident arising from the first attempts to understand what “heat” was.

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, energy is transferred by work when compressing gas with a piston.
Units of Heat

- Historically, the **calorie** was the unit first 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” used for food is actually 1 kilocalorie
- The standard SI unit is the Joule
  - 1 cal = 4.1868 J

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
- 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; i.e. $c = \frac{C}{m}$
- 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, cont.

- The specific heat is 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:
  \[
  Q = m c \Delta T
  \]
  - *Note that the words “Specific Heat” are actually bad terminology. “Specific energy transfer” would be a much better wording to use – but the term is now too entrenched to change!*
Some Specific Heat Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific heat $c$</th>
<th>Specific heat $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J/kg · °C</td>
<td>cal/g · °C</td>
</tr>
<tr>
<td><strong>Elemental solids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>900</td>
<td>0.215</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1830</td>
<td>0.436</td>
</tr>
<tr>
<td>Cadmium</td>
<td>230</td>
<td>0.055</td>
</tr>
<tr>
<td>Copper</td>
<td>387</td>
<td>0.0924</td>
</tr>
<tr>
<td>Germanium</td>
<td>322</td>
<td>0.077</td>
</tr>
<tr>
<td>Gold</td>
<td>129</td>
<td>0.0308</td>
</tr>
<tr>
<td>Iron</td>
<td>448</td>
<td>0.107</td>
</tr>
<tr>
<td>Lead</td>
<td>128</td>
<td>0.0905</td>
</tr>
<tr>
<td>Silicon</td>
<td>703</td>
<td>0.168</td>
</tr>
<tr>
<td>Silver</td>
<td>234</td>
<td>0.056</td>
</tr>
<tr>
<td><strong>Other solids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brass</td>
<td>380</td>
<td>0.092</td>
</tr>
<tr>
<td>Glass</td>
<td>837</td>
<td>0.200</td>
</tr>
<tr>
<td>Ice (−5°C)</td>
<td>2090</td>
<td>0.50</td>
</tr>
<tr>
<td>Marble</td>
<td>860</td>
<td>0.21</td>
</tr>
<tr>
<td>Wood</td>
<td>1700</td>
<td>0.41</td>
</tr>
<tr>
<td><strong>Liquids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol (ethyl)</td>
<td>2400</td>
<td>0.58</td>
</tr>
<tr>
<td>Mercury</td>
<td>140</td>
<td>0.033</td>
</tr>
<tr>
<td>Water (15°C)</td>
<td>4186</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam (100°C)</td>
<td>2010</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Sign Conventions

- If the temperature increases:
  - $Q$ and $\Delta T$ are positive
  - Energy transfers into the system
- If the temperature decreases:
  - $Q$ and $\Delta T$ are negative
  - Energy transfers out of the system
Imagine you have 1 kg each of iron, glass, and water, all at 10°C.

Rank the samples from lowest to highest temperature after 100J of energy is added to each sample.

1. Iron
2. Glass
3. Water

Imagine you have 1 kg each of iron, glass, and water, all at 10°C.

Rank the samples from least to greatest amount of energy transferred by heat if each sample increases temperature by 20°C.

1. Iron
2. Glass
3. Water
Specific Heat (c) Varies With Temperature

- Specific heat actually varies with temperature, with $\Delta Q = mc\Delta T$
- The full equation to use is $Q = m \int_{T_i}^{T_f} c \, dT$
- However, for small temperature intervals, the variation can be ignored and $c$ can be treated as a constant
  - Only $\sim 1\%$ variation in $c$ occurs for water between $0^\circ\text{C}$ and $100^\circ\text{C}$

Specific Heat of Water

- Water has the highest specific heat of common materials
  - Large amount of energy must be exchanged for small temperature changes
- This is responsible for many weather phenomena; e.g.
  - Moderate temperatures near coast
  - Land and sea breezes
Calorimetry

- 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

- Assume the system of the sample and the water is isolated
- Conservation of energy requires that the amount of energy that leaves the sample \( Q_{\text{hot}} \) equals the amount of energy that enters the water \( Q_{\text{cold}} \)
  - Thus \( Q_{\text{cold}} = -Q_{\text{hot}} \)
  - *Notice the minus sign! \( Q_{\text{hot}} \) is negative as the temperature of the hot body falls. Hence \( -Q_{\text{hot}} \) is a positive quantity.*
Calorimetry, final

- Since each $Q = mc\Delta T$, the specific heat $c_s$ for the sample can be found by equating $Q_{cold} = -Q_{hot}$
  
  $$m_w c_w (T_f - T_w) = -m_s c_s (T_f - T_s)$$

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

- $w$ is subscript for the water, $s$ for the sample
- $T_f$ is final temperature of the system
- Technically, the mass of the container should be included, but if $m_w \gg m_{container}$ it can be neglected

Calorimetry, Example

- An ingot of metal is heated and then dropped into a beaker of water. The equilibrium temperature is measured

  $T_w = 20^\circ C$, $T_s = 200^\circ C$, $T_f = 22.4^\circ C$, $m_w = 0.4kg$, $m_s = 0.05kg$

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

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

  $$= 453 \text{ J/kg} \cdot ^\circ \text{C}$$
Specific Heat Capacity for a Gas

- Depends on how the gas is heated:
  - $Q = nC_V \Delta T$ when at constant volume
  - $Q = nC_P \Delta T$ when at constant pressure

- It can also be shown the gas constant
  \[ R = c_p - c_v \]
- We define $\gamma = \frac{c_p}{c_v}$ (the ratio of the specific heats)

Specific Heat for a Gas [cont.]

- For a monatomic gas (a single atom)
  \[ c_v = \frac{3}{2} R, \quad c_p = \frac{5}{2} R \]
  [translational degrees of freedom only]
- For a diatomic gas (e.g. O$_2$, N$_2$)
  \[ c_v = f \, R / 2 \]
  where, for:
  - $0K < T < 100K$, $f=3$, $\gamma = \frac{5}{3}$ (i.e. as monatomic gas)
  - $100K < T < 1,000K$, $f=5$, $\gamma = \frac{7}{5}$ [+rotation]
  - $1,000K < T$, $f=7$, $\gamma = \frac{9}{7}$ [+vibration]
A phase change is when a substance changes from one form to another.

- Two common phase changes are:
  - Solid to liquid (melting)
  - Liquid to gas (boiling)

- During a phase change, there is no change in temperature of the substance.

- We describe the amount of energy required to effect the change by the “Latent Heat”
Latent Heat, $L$

- Different substances react differently to the energy added or removed during a phase change due to their different molecular arrangements.
- The amount of energy also depends on the mass of the sample.
- If an amount of energy $Q$ is required to change the phase of a sample of mass $m$, then $L = \frac{Q}{m}$

Latent Heat, cont

- The quantity $L$ is called the latent heat of the material.
  - 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 $Q = \pm mL$. 
Latent Heat, final

- The *latent heat of fusion* is used when the phase change is from solid to liquid.
- The *latent heat of vaporisation* is used when the phase change is from liquid to gas.
- The positive sign is used when the energy is transferred into the system.
  - This will result in melting or boiling.
- The negative sign is used when energy is transferred out of the system.
  - This will result in freezing or condensation.

### 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>−269.65</td>
<td>$5.23 \times 10^3$</td>
<td>−268.93</td>
<td>$2.09 \times 10^4$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>−209.97</td>
<td>$2.55 \times 10^4$</td>
<td>−195.81</td>
<td>$2.01 \times 10^5$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>−218.79</td>
<td>$1.38 \times 10^4$</td>
<td>−182.97</td>
<td>$2.13 \times 10^4$</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>−114</td>
<td>$1.04 \times 10^5$</td>
<td>78</td>
<td>$8.54 \times 10^5$</td>
</tr>
<tr>
<td>Water</td>
<td>0.00</td>
<td>$3.33 \times 10^5$</td>
<td>100.00</td>
<td>$2.26 \times 10^6$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>119</td>
<td>$3.81 \times 10^4$</td>
<td>444.60</td>
<td>$3.26 \times 10^5$</td>
</tr>
<tr>
<td>Lead</td>
<td>327.3</td>
<td>$2.45 \times 10^4$</td>
<td>1750</td>
<td>$8.70 \times 10^5$</td>
</tr>
<tr>
<td>Aluminium</td>
<td>660</td>
<td>$3.97 \times 10^5$</td>
<td>2450</td>
<td>$1.14 \times 10^7$</td>
</tr>
<tr>
<td>Silver</td>
<td>960.80</td>
<td>$8.82 \times 10^4$</td>
<td>2193</td>
<td>$2.33 \times 10^6$</td>
</tr>
<tr>
<td>Gold</td>
<td>1 063.00</td>
<td>$6.44 \times 10^4$</td>
<td>2660</td>
<td>$1.58 \times 10^6$</td>
</tr>
<tr>
<td>Copper</td>
<td>1 083</td>
<td>$1.34 \times 10^5$</td>
<td>1187</td>
<td>$5.06 \times 10^6$</td>
</tr>
</tbody>
</table>
From Ice to Steam in 5 parts

Part A: Warming Ice

- 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 \( Q = m_i c_i \Delta T \)
  - Find (exercise) that 62.7 J of energy are added
Part B: Melting Ice

- Once at 0ºC, the phase change (melting) starts
- The temperature stays the same although energy is still being added
- Use $Q = m_i L_f$
  - Exercise: find the energy required is 333 J
  - On the graph, the values move from 62.7 J to 396 J

Part C: Warming Water

- Between 0ºC and 100ºC, the material is liquid and no phase changes take place
- Energy added increases the temperature
- Use $Q = m_w c_w \Delta T$
  - Exercise: find that 419 J are added
  - The total energy added is now 815 J
Part D: Boiling Water

- At 100°C, a phase change occurs (boiling)
- Temperature does not change
- Use $Q = m_w L_v$
  - Exercise: find this requires 2260 J
  - The total is now 3070 J

Note that the transition to steam dominates the total amount of energy required in all the 5 parts.

Part E: 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 $Q = m_s c_s \Delta T$
  - Exercise: find that 40.2 J are needed
  - The temperature rises to 120°C
  - The total energy added is 3110 J
Molecular View of Phase Changes

- Phase changes can be described in terms of the rearrangement of molecules (or atoms)
- **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 vaporisation* is the energy required per unit mass to accomplish this separation

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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 vaporisation 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
- YouTube video: Ice melting + Water freezing
Calorimetry: Problem-Solving Strategy

- Units of measurement 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 $Q = mL$
- Be sure to select the correct sign for all energy transfers:
  - Remember to use $Q_{\text{cold}} = -Q_{\text{hot}}$
  - The $\Delta T$ to use is always $T_f - T_i$ (i.e. Final - Initial Temperature)

State Variables

- State variables describe the macroscopic state of a system
  - e.g. Pressure, Temperature, Volume, Internal Energy ($P, T, V, E_{\text{int}}$)
- The macroscopic state of an isolated system can be specified only if the system is in thermal equilibrium internally
Transfer Variables

- For describing changes in state
- 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
- Heat ($Q$) and Work ($W$) are transfer variables
  - Example of heat: we can only assign a value of the heat if energy crosses a boundary

Work in Thermodynamics

- Work can be done on a deformable system, such as a gas
- Consider a cylinder with a moveable piston
- Suppose a force is applied to slowly compress the gas
  - The compression is slow enough for the system to remain essentially in thermal equilibrium
  - This is said to occur quasi-statically
Work done on the Gas

- The piston is pushed downward by a force $F$ through a displacement of $dr$
  \[ dW = F \cdot dr = -Fdy = -PAdy \]
- Since pressure $P = F/A$
- Change in volume of the gas $dV = A \cdot dy$
- Thus work done on gas $dW = -P dV$

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

See Active Figure 20.04

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

PV Diagrams, cont

Since $dW = -PdV$, 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
Work Done By Various Paths

- See Active Figure 20.05
- Each of these processes has the same initial and final states
- The work done differs in each process
- The work done depends on the path

Work From a $PV$ Diagram: 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 $PV$ Diagram: 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 $PV$ Diagram: 3

- The pressure and the volume continually change
- The work is some intermediate value 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
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.

- Reservoir in thermal contact with Gas
- The piston is pulled upwards, the gas is doing work on the piston
Heat Transfer, Example 2

- In this example the gas has the same initial volume, temperature and pressure as in the previous example.
- Completely thermally insulated however.
- The membrane is broken and the gas expands rapidly into the evacuated region.
- The final states, $V_f$ & $P_f$, in the PV-diagram are also identical.
- No energy is transferred by heat through the insulating wall.
- No work is done by the gas expanding into the vacuum.

Example 1 vs. Example 2

- Initial values of $P$, $V$, $n$ & $T$ the same in both cases.
- Final values of $n$ & $V$ also the same in both cases.
- $T_{\text{init}} = T_{\text{final}}$ in both cases (by design of the experiments).
  - So no change in internal energy; i.e. $\Delta E=0$
- Thus, from ideal gas eqn. final values of $P$ the same in both cases (with $P_{\text{final}} = P_{\text{init}}/2$).
- Thus, final values of $P$, $V$, $n$ & $T$ the same in both cases.  
  - But we get there by very different processes!
- Example 1: Work done by the gas, and heat flows into it.
  - From conservation of energy $\Delta W=-\Delta Q$
- Example 2: No work done by the gas, no heat flows into the system.  So $\Delta W=0$, $\Delta Q=0$
Energy Transfer, Summary

- Case 1: gas does work on the piston and energy slowly transferred to gas by heat.
- Case 2: no energy transferred by heat, and no work is done.
- But the initial and final states in PV-diagram are the same in both cases!
- Energy transfers by heat, like the work done, depend on the initial, final, and intermediate states of the system.
- Both work and heat depend on the path taken.
- Neither can be determined solely by the end points of thermodynamic process.
  - Need a principle to incorporate this.......

The First Law of Thermodynamics

- A special case of Conservation of Energy
  - It takes into account changes in internal energy and energy transfers by heat and work
  - Although $Q$ and $W$ each are dependent on the path, $Q + W$ is independent of the path
  - The First Law of Thermodynamics states that
    \[ \Delta E_{\text{int}} = Q + W \]
    - $Q$ is the energy transfer in the system
    - $W$ is the work done on the gas
    - $\Delta E_{\text{int}}$ is the change in its internal energy
The First Law of Thermodynamics, cont.

- One consequence of the first law is that there must exist some quantity known as internal energy which is determined by the state of the system.
- For infinitesimal changes in a system:
  - \( dE_{\text{int}} = dQ + dW \)
- The first law is an energy conservation statement specifying that the only type of energy that changes in a system is the internal energy.

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 \( \Delta E_{\text{int}} = 0 \)
- 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 since it is a state variable
- If $\Delta E_{\text{int}} = 0$, then $Q = -W$
- 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
  - e.g. Engines

Some Processes

Active Figure 20.07

- Adiabatic
  - No energy leaves or enters, $Q=0$
- Isobaric
  - Constant pressure, $P=\text{constant}$.
- Isovolumetric
  - Constant volume, $V=\text{constant}$.
- Isothermal
  - Constant temperature, $T=\text{constant}$.
As the gas expands rapidly it cools, leading to condensation and cloud formation.

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
Adiabatic Process, cont.

- Since $Q = 0$, $\Delta E_{\text{int}} = Q + W = W$
- If the gas is compressed adiabatically, $W$ is positive so $\Delta E_{\text{int}}$ is positive and the temperature of the gas increases.
- If the gas expands adiabatically, the temperature of the gas decreases.
- Can also show that $PV^\gamma$=constant for an adiabatic process, where $\gamma$ is a constant for a particular gas.
  - $\gamma = c_p/c_v$, the ratio of specific heats for an ideal gas at constant pressure and constant volume.
  - See §19.9 of Haliday, Resnick & Walker for proof (not examinable)

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$PV^\gamma$=const. for Adiabatic Change

Outline of Proof (§19.9 HR&W)

- Not for examination!
- Two concepts for an ideal gas:
  - $C_p$ specific heat capacity at constant pressure
  - $C_v$ specific heat capacity at constant volume
- It can be shown that $dE=n c_v dT$ and $R=c_p-c_v$
- Combine $dE=-PdV$ (since $dQ=0$) with $PV=nRT$
  - So that $PdV + VdP = nRdT$
- To yield $PV^\gamma = \text{constant}$, where $\gamma=c_p/c_v$
Adiabatic Processes, Examples

- Some important examples of adiabatic processes related to engineering are:
  - The expansion of hot gases in an internal combustion engine
  - The liquefaction of gases in a cooling system
  - The compression stroke in a diesel engine
  - *See your Engineering courses!*

Adiabatic Free Expansion

- Break the membrane so the gas expands to fill the vacuum. An example of adiabatic free expansion.
- The process is adiabatic because it takes place in an insulated container.
- No work is done, so $W = 0$
- Since $Q = 0$ and $W = 0$, $\Delta E_{\text{int}} = 0$ and the initial and final energies are the same
  - Hence no change in temperature occurs.
**Isobaric Processes**

- An isobaric process is one that occurs at a constant pressure.
- The values of the heat and the work terms are generally both non-zero.
- The work done is $W = -P (V_f - V_i)$ where $P$ is the constant pressure.

**Isovolumetric Processes**

- An isovolumetric process is one in which there is no change in the volume.
- Since the volume does not change: $W = -PdV = 0$
- Thus, from the first law, $\Delta E_{int} = Q$
- Hence, 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.
**Isothermal Process**

- An isothermal process is one that occurs at a constant temperature.
- Since there is no change in temperature, $\Delta E_{\text{int}} = 0$.
- Therefore, from First Law, $Q = -W$.
- Any energy that enters the system by heat must leave the system by work.

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

In the empty columns of the table, fill in the correct signs ($-, +, 0$) for $Q$, $W$ and $\Delta E_{\text{int}}$.

<table>
<thead>
<tr>
<th>Situation</th>
<th>System</th>
<th>$Q$</th>
<th>$W$</th>
<th>$\Delta E_{\text{int}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Rapidly pumping up a bicycle tyre</td>
<td>Air in the pump</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Pan of room temperature water sitting on a hot stove</td>
<td>Water in the pan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Air leaking quickly out of a balloon</td>
<td>Air originally in the balloon</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Isothermal Process PV-diagram

- At right is a \( PV \) diagram of an isothermal expansion.
- The curve is a hyperbola, since \( PV = \text{constant} \).
- The curve is called an isotherm.

Isothermal Expansion, Details

- \( PV = nRT = \text{constant} \) when isothermal
  - The equation of a hyperbola
- Because it is an ideal gas and the process is quasi-static, \( PV = nRT \) and

\[
W = -\int_{V_i}^{V_f} P \, dV = -\int_{V_i}^{V_f} \frac{nRT}{V} \, dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}
\]

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

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

Special Processes, Summary

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

- Adiabatic
  - No heat exchanged
  - $Q = 0$ and $\Delta E_{\text{int}} = W$
  - $PV^\gamma$ = constant
- Isovolumetric
  - Constant volume
  - $W=0$ so $\Delta E_{\text{int}} = Q$
- 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 $Q = -W$
  - $PV = \text{constant}$, $W = nRT \ln(V_f/V_i)$
WEM05VD3: Heat converted to Work Done

36 seconds

HB10 Thermal Conductivity

- When the centre block is heated the different rates of thermal conductivity are shown by the rate that the flags, which are attached with wax, drop.

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$ W/m/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>397</td>
</tr>
<tr>
<td>Al</td>
<td>237</td>
</tr>
<tr>
<td>Brass</td>
<td>109</td>
</tr>
<tr>
<td>Steel</td>
<td>40</td>
</tr>
</tbody>
</table>
We want to know the rate at which energy is transferred.

There are various mechanisms responsible for the transfer:
- Conduction
- Convection
- Radiation

**Conduction**

- View transfer on an atomic scale
  - 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 near the heat source vibrate with larger amplitudes
- These collide with adjacent molecules and transfer some energy
- Eventually, the energy travels entirely through the pan

Conduction, cont.

- In general, metals are good 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 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.
- Rate of energy transfer is given by
  \[ P = \kappa A \frac{dT}{dx} \]

Conduction, equation explanation

- \( A \) is the cross-sectional area
- \( \Delta x \) is the thickness of the slab
  - Or the length of a rod
- \( P \) is in Watts when \( Q \) is in Joules
- \( \kappa \) is the thermal conductivity of the material
  - Good conductors have high \( \kappa \) values and good insulators have low \( \kappa \) values
Temperature Gradient

- The quantity $|dT/dx|$ 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:
- Thus, the rate of energy transfer becomes:

\[ P = \kappa A \frac{T_h - T_c}{L} \]

Some Thermal Conductivities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Thermal Conductivity (W/m \cdot °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals (at 25°C)</strong></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>
<tr>
<td><strong>Gases (at 20°C)</strong></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>
<tr>
<td><strong>Nonmetals (approximate values)</strong></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>2,900</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>
Quick Quiz

In which case is the rate of energy transfer by heat larger?

- (a) When the rods are in Series
- (b) When the rods are in Parallel

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, 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

- Power $P = \sigma A e T^4$
  - $P$ is the rate of energy transfer, in Watts
  - $\sigma = 5.6696 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$
  - $A$ 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 Kelvins

Energy Absorption and Emission by Radiation

- With its surroundings, the rate at which the object at temperature $T$ with surroundings at $T_s$ radiates is
  - $P_{\text{net}} = \sigma A e (T^4 - T_s^4)$
  - When an object is in equilibrium with its surroundings, it radiates and absorbs at the same rate
    - Its temperature will not change
Ideal Absorbers and Reflectors

- An *ideal absorber* is defined as an object that absorbs all of the energy incident on it
  - $e = 1$
  - This type of object is called a **black body**
  - An ideal absorber is also an ideal radiator of energy
- An *ideal reflector* absorbs none of the energy incident on it
  - $e = 0$

ABC Lateline discovers the First Law of Thermodynamics
Explanations

(a) Pumping rapid, so $Q=0$. $W>0$ when work done on system, as here. Thus $\Delta E_{\text{int}} > 0$, and so air in pump warmer too.

(b) No work done on system, but energy transfers in, so $Q>0$. Thus $\Delta E_{\text{int}} > 0$ too, as water gets hotter.

(c) No energy transfer so $Q=0$. Air molecules escaping from balloon do work pushing their way out, so $W<0$. Thus $\Delta E_{\text{int}} < 0$ too. Decrease is also evident because the escaping air becomes colder.

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