Lecture 35

- The laws of thermodynamics
  - The 1st Law of Thermodynamics
  - Thermodynamics of Ideal Gas
Last lecture:

1. Thermal physics
   ✓ Heat transfer.

**Review Problem:** Lead pellets, each of mass 1.00 g, are heated to 200°C. How many pellets must be added to 500 g of water that is initially at 20.0°C to make the equilibrium temperature 25.0°C? Neglect any energy transfer to or from the container.
Lead pellets, each of mass 1.00 g, are heated to 200°C. How many pellets must be added to 500 g of water that is initially at 20.0°C to make the equilibrium temperature 25.0°C? Neglect any energy transfer to or from the container.

Note: $c_{\text{lead}}=128 \text{ J/kg°C}$, $c_{\text{water}}=4186 \text{ J/kg°C}$
Work in Thermodynamic Processes – State Variables

• State of a system
  • Description of the system in terms of state variables
    • Pressure
    • Volume
    • Temperature
    • Internal Energy

• A macroscopic state of an isolated system can be specified only if the system is in internal thermal equilibrium
Work

- Work is an important energy transfer mechanism in thermodynamic systems
- Heat is another energy transfer mechanism

Example: gas cylinder with piston
- The gas is contained in a cylinder with a moveable piston
- The gas occupies a volume $V$ and exerts pressure $P$ on the walls of the cylinder and on the piston
Work in a Gas Cylinder

• A force is applied to slowly compress the gas
  • The compression is slow enough for all the system to remain essentially in thermal equilibrium

\[ W = -P \Delta V \]

• This is the work done \textit{on} the gas
Work on a Gas Cylinder

\[ W = -P \Delta V \]

- When the gas is compressed
  - \( \Delta V \) is negative
  - The work done on the gas is positive
- When the gas is allowed to expand
  - \( \Delta V \) is positive
  - The work done on the gas is negative
- When the volume remains constant
  - No work is done on the gas
Notes about the Work Equation

\[ W = -P \Delta V \]

- If the pressure remains constant during the expansion or compression, the process is called an \textit{isobaric} process.
- If the pressure changes, the average pressure may be used to estimate the work done.

\[ W = -P \Delta V \]

Work done \textit{on} the gas

Work=Area under the curve
PV Diagrams

- Used when the pressure and volume are known at each step of the process
- The work done on a gas that takes it from some initial state to some final state is the negative of the area under the curve on the PV diagram
  - This is true whether or not the pressure stays constant
PV Diagrams

- The curve on the diagram is called the path taken between the initial and final states.
- The work done depends on the particular path.
  - Same initial and final states, but different amounts of work are done.
Find work done by the gas in this cycle.
Find work done by the gas in this cycle.

Note: work is equal to the area:

\[ W = (p_2 - p_1)(V_2 - V_1) \]
Other Processes

• **Isovolumetric**
  • Volume stays constant
  • Vertical line on the PV diagram

• **Isothermal**
  • Temperature stays the same

• **Adiabatic**
  • No heat is exchanged with the surroundings

\[
W = nRT \ln \left( \frac{V_f}{V_i} \right) = P_i V_i \ln \left( \frac{V_f}{V_i} \right)
\]
Example: Calculate work done by expanding gas of 1 mole if initial pressure is 4000 Pa, initial volume is 0.2 m³, and initial temperature is 96.2 K. Assume a two processes: (1) *isobaric* expansion to 0.3 m³, $T_f$=144.3 K (2) *isothermal* expansion to 0.3 m³.

**Given:**
- $n = 1$ mole
- $T_i = 96.2 \text{ K}$
- $T_f = 144.3 \text{ K}$
- $V_i = 0.2 \text{ m}^3$
- $V_f = 0.3 \text{ m}^3$
- $P = \text{const}$

**Find:**
- $W = ?$

1. **Isobaric expansion:**

$$W = P\Delta V = P(V_f - V_i) = 4000 \text{ Pa} \left(0.3 \text{ m}^3 - 0.2 \text{ m}^3\right) = 400 \text{ J}$$

Also:

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} \frac{1}{nR} = \frac{V_f}{V_i} = \frac{0.3 \text{ m}^3}{0.2 \text{ m}^3} = 1.5$$

A 50% increase in temperature!
Example:

Calculate work done by expanding gas of 1 mole if initial pressure is 4000 Pa, initial volume is 0.2 m³, and initial temperature is 96.2 K. Assume a two processes: (1) *isobaric* expansion to 0.3 m³, T_f=144.3 K (2) *isothermal* expansion to 0.3 m³.

Given:

- \( n = 1 \) mole
- \( T_i = 96.2 \) K
- \( V_i = 0.2 \) m³
- \( V_f = 0.3 \) m³
- \( T = \text{const} \)

Find:

\( W = ? \)

2. **Isothermal** expansion:

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

\[
= (4000 \text{ Pa}) (0.2 m^3) \ln \frac{0.3 m^3}{0.2 m^3} = 324 \text{ J}
\]

Also:

\[
P_f = P_i \frac{V_i}{V_f} = 4000 \text{ Pa} \frac{0.2 m^3}{0.3 m^3} = 2667 \text{ Pa}
\]

A ~67% decrease in pressure!
Processes for Transferring Energy

How can energy be transferred?

- By doing work
  - Requires a macroscopic displacement of the point of application of a force
- By heat
  - Occurs by random molecular collisions
- Results of both
  - Change in internal energy of the system
  - Generally accompanied by measurable macroscopic variables
    - Pressure
    - Temperature
    - Volume
First Law of Thermodynamics

- Consider energy conservation in thermal processes. Must include:
  - $Q$
    - Heat
    - Positive if energy is transferred to the system
  - $W$
    - Work
    - Positive if done on the system
  - $U$
    - Internal energy
    - Positive if the temperature increases
First Law of Thermodynamics

• The relationship among U, W, and Q can be expressed as

\[ \Delta U = U_f - U_i = Q + W \]

• This means that the change in internal energy of a system is equal to the sum of the energy transferred across the system boundary by heat and the energy transferred by work
Applications of the First Law:
1. Isolated System

- An *isolated system* does not interact with its surroundings
- No energy transfer takes place and no work is done
- Therefore, the internal energy of the isolated system remains constant
Example:

If 500 J of heat added to ideal gas that is expanding from 0.2 m$^3$ to 0.3 m$^3$ at a constant pressure of 4000 Pa, what is the change in its internal energy?

**Given:**

- $n = 1$ mole
- $V_i = 0.2$ m$^3$
- $V_f = 0.3$ m$^3$
- $P = \text{const}$
- $Q = 500$ J

**Find:**

- $\Delta U =$?

1. **Isobaric expansion:**

   $$W = P\Delta V = P(V_f - V_i) = 4000 \text{ Pa}(0.3\text{m}^3-0.2\text{m}^3)$$
   $$= 400 \text{ J}$$

   Use 1st law of thermodynamics:

   $$Q = \Delta U + W$$
   $$\Delta U = Q - W = 500 \text{ J} - 400 \text{ J} = 100 \text{ J}$$
Applications of the First Law:

2. Cyclic Processes

• A cyclic process is one in which the process originates and ends at the same state

\[ U_f = U_i \text{ and } Q = -W \]

• The net work done per cycle by the gas is equal to the area enclosed by the path representing the process on a PV diagram
Example: Cyclic Process in a PV Diagram

- This is an ideal monatomic gas confined in a cylinder by a moveable piston
- A to B is an isovolumetric process which increases the pressure
- B to C is an isothermal expansion and lowers the pressure
- C to A is an isobaric compression
- The gas returns to its original state at point A
Applications of the First Law:

3. Isothermal Processes

- Isothermal means constant temperature
- The cylinder and gas are in thermal contact with a large source of energy
- Allow the energy to transfer into the gas (by heat)
- The gas expands and pressure falls to maintain a constant temperature ($\Delta U = 0$)
- The work done is the negative of the heat added

\[
W = nRT \ln \left( \frac{V_i}{V_f} \right).
\]
Applications of the First Law:
4. Adiabatic Process

- Energy transferred by heat is zero
- The work done is equal to the change in the internal energy of the system
- One way to accomplish a process with no heat exchange is to have it happen very quickly
- In an adiabatic expansion, the work done is negative and the internal energy decreases
Applications of the First Law:
5. Isovolumetric (Isochoric) Process

- No change in volume, therefore no work is done
- The energy added to the system goes into increasing the internal energy of the system
  - Temperature will increase

\[ Q = \Delta U = nC_V \Delta T. \]
Applications of the First Law: 6. Isobaric Process

For a constant pressure (isobaric) process, the change in internal energy is

$$\Delta U = Q + W$$

where

$$W = -P \Delta V = -nR\Delta T$$  and  $$Q = nC_p \Delta T.$$  

\(C_p\) is the molar specific heat at constant pressure. For an ideal gas \(C_p = C_V + R\).
Example: An ideal monatomic gas is taken through a cycle in the PV diagram.
(a) If there are 0.0200 mol of this gas, what are the temperature and pressure at point C? (b) What is the change in internal energy of the gas as it is taken from point A to B? (c) How much work is done by this gas per cycle? (d) What is the total change in internal energy of this gas in one cycle?

From the graph: \( P_c = 98.0 \text{ kPa} \)

Using the ideal gas law

\[
T_c = \frac{P_c V_c}{nR} = 1180 \text{ K.}
\]
Example continued:

(b) What is the change in internal energy of the gas as it is taken from point A to B?

This is an isochoric process so \( W = 0 \) and \( \Delta U = Q \).

\[
\Delta U = Q = nC_v \Delta T = n \left( \frac{3}{2} R \right) \left( \frac{P_B V_B}{nR} - \frac{P_A V_A}{nR} \right) \\
= \frac{3}{2} \left( P_B V_B - P_A V_A \right) \\
= \frac{3}{2} V \left( P_B - P_A \right) = -200 \text{ J}
\]
Example continued:

(c) How much work is done by this gas per cycle?

The work done per cycle is the area between the curves on the PV diagram. Here \( W = \frac{1}{2} \Delta V \Delta P = 66 \text{ J} \).

(d) What is the total change in internal energy of this gas in one cycle?

\[
\Delta U = nC_v \Delta T = n \left( \frac{3}{2} R \right) \left( \frac{P_f V_f}{nR} - \frac{P_i V_i}{nR} \right) = \frac{3}{2} (P_f V_f - P_i V_i) = 0
\]

The cycle ends where it began (\( \Delta T = 0 \)).