Lecture 7: Thermo and Entropy

• Reading: Zumdahl 10.2, 10.3

• Outline
  – Isothermal processes
  – Isothermal gas expansion and work
  – Reversible Processes
Isothermal Processes

• Recall: Isothermal means $\Delta T = 0$.

• Since $\Delta E = nC_v\Delta T$, then $\Delta E = 0$ for an isothermal process.

• Since $\Delta E = q + w$:

  $q = -w$ (isothermal process)

  Heat goes into a machine and it does work ($q$, and $-w$ are both positive).
Example: Isothermal Expansion

- Consider a mass connected to a ideal gas contained in a “piston”. Piston is submerged in a constant T bath such that $\Delta T = 0$ during expansion.
Isothermal Expansion: Start

\[ \Delta V = A \Delta h \]

\[ PV = P_1 V_2 = nRT \]

- Initially, \( V = V_1 \)
  \( P = P_1 \)

- Pressure of gas is equal to that created by mass:

\[ P_1 = \text{force/area} = M_1 g / A \]

where \( A = \text{piston area} \)

\( g = \text{gravitational acceleration} \ (9.8 \text{ m/s}^2) \)
Isothermal Expansion: One Step
(Not Reversible or Irreversible)

• One-Step Expansion. We change the weight to $M_1/4$, then

$$P_{\text{ext}} = (M_1/4)g/A = P_1/4$$

Internal pressure is larger than the external pressure so the gas will expand. The work done is defined by the pressure on the yielding side (external).

• The mass will be lifted until the internal pressure equals the external pressure. In this case

$$V_{\text{final}} = 4V_1$$

• Because

$$nRT = PV = P_1V_1 = P_{\text{final}}V_{\text{final}}$$

• $q = -w = P_{\text{ext}}\Delta V = P_1/4 (4V_1 - V_1) = 3/4 P_1V_1$
Two Step Expansion

- In this expansion we go in two steps:
  
  Step 1: $M_1$ to $M_1/2$
  Step 2: $M_1/2$ to $M_1/4$

- Step 1:

  $P_{ext} = P_{1/2}$, $V_{final} = 2V_1$

- $-w_1 = P_{ext} \Delta V = P_{1/2} (2V_1 - V_1) = 1/2 P_1 V_1$
Two Step Expansion: Second Step

- In Step 2 (Move $M_1/2$; then move $M_1/4$):
  
  $$P_{\text{ext}} = P_1/4, \ V_{\text{final}} = 4V_1$$

- $w_2 = P_{\text{ext}} \Delta V = P_1/4 \ (4V_1 - 2V_1) = 1/2 \ P_1 V_1$

- $w_{\text{total}} = -(w_1 + w_2) = P_1 V_1/2 + P_1 V_1/2 = P_1 V_1$

$$-w^{2\text{steps}}_{\text{total}} = P_1 V_1 = nRT > \frac{3}{4} P_1 V_1 = -w^{1\text{step}}_{\text{total}}$$

Get more work (but use more heat) to move the weights in 2 steps than a single step. In the two step the second weight is raised to exactly the same height and the single step and an additional weight is moved half the distance.
Graph: Two Step Expansion

- Work is given by the area under the “PV” curve.
Graph: Two Step and One Step Expansion

- See both expansion processes on a PV diagram:

- Work is given by the area under the “PV” curve.
Graphical: Infinite Step Expansion

Two Step:  
Irreversible

Reversible
Infinite Step Expansion

• Imagine that we perform a process in which we change the weight “infinitesimally” between expansions.

• A very small weight is removed and the pressure inside the box is nearly the same as the external pressure.

• Instead of determining the sum of work performed at each step to get $w_{\text{total}}$, we integrate:

$$w = - \int_{V_{\text{initial}}}^{V_{\text{final}}} P_{\text{ex}} \, dV = - \int_{V_{\text{initial}}}^{V_{\text{final}}} P \, dV = - \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{nRT}{V} \, dV$$
Many Step Expansion

Break up \( \frac{3}{4} \) of the weight into many (N) small weights and take each small weight off one at a time. Consider a single step in the middle of the process, and then add up all steps.

\[
N \Delta m = \frac{3}{4} M \\
m_1 = m_2 + \Delta m \\
P_1 V_1 = P_2 V_2 = nRT \\
V_2 = V_1 + \Delta V \\
P_1 = \frac{m_1 g}{A} = P_2 + \frac{\Delta mg}{A} \\
\left( P_2 + \frac{\Delta mg}{A} \right) V_1 = P_2 \left( V_1 + \Delta V \right) \\
-w_1 = P_2 \Delta V = \left( \frac{\Delta mg}{A} \right) V_1 = nRT \frac{\Delta m}{m_1} \\
m_i = M - (i - 1) \Delta m \\
\sum_{i=1}^{N} (-w_i) = nRT \sum_{i=1}^{N} \frac{\Delta m}{M - (i - 1) \Delta m} \\
-w_{Total} = nRT \left\{ \sum_{i=1}^{N} \frac{1}{\frac{4}{3} N - (i - 1)} \right\}
The work as $N$ becomes large; many small steps

We have divided the weights a bit differently (from the two step) but we can compare 1, 2, 3 and an infinite number of steps, by doing the sum for different values of $N$:

\[
N \quad \sum_{i=1}^{N} \frac{1}{\frac{4}{3} N - (i - 1)}
\]

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\sum_{i=1}^{N} \frac{1}{\frac{4}{3} N - (i - 1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\frac{3}{4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.975</td>
</tr>
<tr>
<td>1000</td>
<td>1.385</td>
</tr>
</tbody>
</table>
Reversible Isothermal Expansion:  
(Infinite number of steps; can go back and forth)

- Add up areas (integrate) from $V_1$ to $V_2$

$$w_{total} = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT(\ln(V)) \bigg|_{V_1}^{V_2} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$q_{rev} = -w_{rev} = nRT \ln \left( \frac{V_2}{V_1} \right)$$
Compare Work for different steps

- One step \( q_{1\,step} = \frac{3}{4} PV \)
- Two \( q_{2\,steps} = PV \)
- Infinite Number of Steps:
  \[ q_{\text{revers}} = PV \ln(4) = 1.386PV \]
  \( q_{\text{reversible}} > q_2 > q_1 \)
One Step Compression

State of the system after the 1 Step Expansion:

\[ V_{\text{initial}} = 4V_1 \quad P_{\text{initial}} = \frac{1}{4} P_1 \]

What do we have to do to get the system back to its original state before 1-step expansion? [Pick up Weight]

System did work: Raised \( M/4 \); to restore it we have to raise \( 3M/4 \) the same distance. We must do more work to restore the system than we got from it in the first place.
Two Step Compression

State of the system after the 2 Step Expansion:

\[ V_{\text{initial}} = 4V_1 \quad P_{\text{initial}} = \frac{1}{4} P_1 \]

What do we have to do to get the system back to its original state before 2-step expansion? [Pick Weights Up]

Compression in two steps:
first: place on mass \( M_1/4 \), second: then \( M_1/2 \) on pan.
Two Step Compression:
Compare work done by system with work we need to
do to restore the system

• To expand the system did total work \( (P_1V_1) \)
• To compress: In first step: we need to move weight \( \frac{M_1}{4} \)
  up to the pan and use that pressure to compress the gas

\[
P_{\text{step1}}^{2\text{Step}} = \frac{1}{2} M_1 \frac{g}{A} = \frac{1}{2} P_1 \quad \Delta V_{\text{step1}}^{2\text{Step}} = 2V_1 - 4V_1 = -2V_1
\]

\[
w_{\text{step1}}^{2\text{Step}} = -P_{\text{step1}}^{2\text{Step}} \Delta V_{\text{step1}}^{2\text{Step}} = \frac{1}{2} P_1 \cdot 2V_1 = P_1V_1
\]

Second step is similar and the same work is done on the system.

However, we do not know how much of the work we did ended up as heat into the reservoir or heat into the weights as they dropped. We just know that to compress it back to (approximately) its original state it took twice as much compression work (not counting the extra work we did to move the weights) to compress as it did to expand.
Compression/Expansion

The system is the gas in the box and does not include the weights in the environment. The weights help us keep track of the work.

• In two step example:
  \[ w_{\text{expan.}} = -P_1 V_1 \]
  \[ w_{\text{comp.}} = 2P_1 V_1 \]
  \[ w_{\text{total}} = P_1 V_1 \]
  \[ q_{\text{total}} = -P_1 V_1 \]

• We have undergone a “cycle” where the system returns to the starting state.

• Now, \( \Delta E = 0 \) (state fxn)

\[ q_{\text{total}} = -w_{\text{total}} \neq 0 \]
A Thermodynamic Engine: Defining Entropy

Imagine doing all steps reversibly, then compression is simpler to understand. The system variables (P,T) are always only incrementally different from the external values.

Use two different heat reservoirs at two different temperatures.

Let’s consider the four-step cycle illustrated:

- 1: Isothermal expansion
- 2: Isochoric cooling
- 3: Isothermal compression
- 4: Isochoric heating
First Step of Four Cycle

- **Step 1:** Isothermal Expansion at $T = T_{\text{high}}$ from $V_1$ to $V_2$

- Now $\Delta T = 0$; therefore, $\Delta E = 0$ and $q = -w$

- Do expansion reversibly. Then:

$$q_1 = -w_1 = nRT_{\text{high}} \ln \left( \frac{V_2}{V_1} \right)$$
Step 2

- Step 2: Isochoric Cooling to $T = T_{\text{low}}$.
- Now $\Delta V = 0$; therefore, $w = 0$
- $q_2 = \Delta E = nC_v \Delta T$
  \[ = nC_v(T_{\text{low}} - T_{\text{high}}) \]
Step 3

- Step 3: Isothermal Compression at $T = T_{\text{low}}$ from $V_2$ to $V_1$.

- Now $\Delta T = 0$; therefore, $\Delta E = 0$ and $q = -w$

- Do compression reversibly, then

$$q_3 = -w_3 = nRT_{low} \ln \left( \frac{V_1}{V_2} \right)$$
Step 4

- Step 4: Isochoric Heating to $T = T_{\text{high}}$.

- Now $\Delta V = 0$; therefore, $w = 0$

- $q_4 = \Delta E = nC_v \Delta T$
  
  $$= nC_v (T_{\text{high}} - T_{\text{low}}) = -q_2$$
All 4 steps of the engine, added together

\[ q_{total} = q_1 + q_2 + q_3 + q_4 \]

\[ q_{total} = q_1 + q_3 \]

\[ q_{total} = nR T_{\text{high}} \ln \left( \frac{V_2}{V_1} \right) + nR T_{\text{low}} \ln \left( \frac{V_1}{V_2} \right) \]

\[ q_{total} = nR T_{\text{high}} \ln \left( \frac{V_2}{V_1} \right) - nR T_{\text{low}} \ln \left( \frac{V_2}{V_1} \right) \]

\[ q_{total} = nR \Delta T \ln \left( \frac{V_2}{V_1} \right) = -w_{total} \]
Defining Entropy

\[ q_{total} = nRT_{high} \ln \left( \frac{V_2}{V_1} \right) - nRT_{low} \ln \left( \frac{V_2}{V_1} \right) \]

Because this quantity is zero when summed over all changes which brings the system back to where it started, is zero it must depend on the state of the system and so is a state function.

Thermodynamic definition of entropy: The heat transferred under reversible conditions divided by the temperature. What if the transfer is not reversible? Then the amount of heat transferred is not the same but the entropy is the same.
Calculating Entropy

\[ \Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{rev}}}{T} \]

\[ \Delta T = 0 \quad q_{\text{rev}} = nRT \frac{\Delta V}{V} \quad \Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{rev}}}{T} = nR \ln \left( \frac{V_{\text{final}}}{V_{\text{initial}}} \right) \]

\[ \Delta V = 0 \quad q_{\text{rev}} = nC_v \Delta T \quad \Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{rev}}}{T} = nC_v \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right) \]

\[ \Delta P = 0 \quad q_{\text{rev}} = nC_p \Delta T \quad \Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{rev}}}{T} = nC_p \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right) \]
Calculating Entropy

- Example: What is $\Delta S$ for the heating of a mole of a monatomic gas isochorically from 298 K to 350 K?

$$\Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{rev}}}{T} = nC_v \ln \left( \frac{T_{\text{final}}}{T_{\text{initial}}} \right)$$

$$= \frac{3}{2} R$$

$$\Delta S = (1 \text{ mol}) \left( \frac{3}{2} R \right) \ln \left( \frac{350 K}{298 K} \right)$$

$$\Delta S = 2 \frac{J}{K}$$
Connecting with Lecture 6

• From this lecture:

$$\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T} = \frac{q_{rev}}{T} = \frac{nRT}{T} \ln \left( \frac{V_{final}}{V_{initial}} \right) = nR \ln \left( \frac{V_{final}}{V_{initial}} \right)$$

• Exactly the same as derived in the previous lecture!

$$\Delta S = Nk \ln \left( \frac{V_{final}}{V_{initial}} \right) = nR \ln \left( \frac{V_{final}}{V_{initial}} \right)$$