Lecture 9 – Chapt 7 (second half) PV work.

Outline:
System and Surroundings
First Law  \[ \Delta U = q + w \]
Expansion Work
1. Free expansion
2. Isothermal, constant P
3. Isothermal reversible
4. Adiabatic expansion

Quick review:
We will quickly get through to our fundamental thermodynamic equations for S and U.

Begin with definitions
\[ S = S(U,V,N) \]
\[ U = U(S,V,N) \]

We can then easily define \( dS \) and \( dU \).
\[
\begin{align*}
    dS &= \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \sum_i \left( \frac{\partial S}{\partial N_i} \right)_{U,V,N_{\text{pes}}} dN_i \\
    dU &= \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \sum_i \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_{\text{pes}}} dN_i
\end{align*}
\]

and we define the coefficients as familiar driving forces
\[
\begin{align*}
    dS &= \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i \\
    dU &= TdS - pdV + \sum_i \mu_i dN_i
\end{align*}
\]
Remember with thermodynamics, we are keeping track of energy as it flows around. While ago I put up these sketches of heat and work from a microscopic perspective. Remember?

We can think of energy as the capacity to do work. Heat is energy that is transferred by a temperature gradient.

**Today we will get into several descriptions of energy flow using the first law.**

One final point about work and energy before we get rolling is how we define what is positive. The **system** is our set of particles of interest. In the above example it is the gas inside the piston. The **surroundings** is everything else. **Positive work, then, is work done on the system by the surroundings.** This is positive because work in this direction increases the energy of the system.

OK then, so let’s recall the **First law of Thermodynamics:** The internal energy of an isolated system is constant.

\[ \Delta U = q + w \]

In other words: energy is neither produced or consumed. In yet another way, \( q \) and \( w \) are the only ways to change energy.

As pointed out by Abby last week, note that \( q \) and \( w \) are **what kinds of functions?** path fnctns **But their sum is a?** state fnctn.

One common kind of work:
Expansion work: work arising from a change in volume. This takes place in internal combustion engines. So, why not picture this as a gas expanding against a piston.
Work = force x distance  
\[ dw = Fdz \] (multiply by A / A)  
\[ dw = F_{ext} / A \ A \ dz \]  
\[ F/A = p \]  
\[ dw = p_{ext} A \ dz \]  
\[ Adz = dV \]  
\[ dw = p_{ext} dV \]  
as this is, we have the piston doing work on the system. So, we need to reverse this. And if \( p \) isn’t constant we need to integrate.  
\[ \int dw = -\int p_{ext} dV \]  

Armed with this equation, let’s look at several specific types of expansion work

1. **Free Expansion**: \( p_{ext} = 0 \). There is no force opposing the expansion. Therefore, \( dw = 0 \) for each stage of expansion and \( w \) = 0 overall.  
\[ -\int 0 \ dV = 0 \]  

This makes sense because it takes no effort to push against nothing. Also, if there is nothing to push against, then we aren’t transferring energy to any particles outside the piston.

2. **Isothermal expansion against constant pressure**: \( p_{ext} \) is constant throughout the expansion, so our integral is easy to evaluate:  
\[ w = -\int P_{ext} \ dV \]  
\[ = -P_{ext} \int dV \]  
\[ = -P_{ext} \Delta V \]  

We’ll show later that  
\[ \Delta U = \int_{V_1}^{V_2} C_v \ dT \]  

(and if \( C_v \) is constant?  
\[ \Delta U = C_v \Delta T \]  

so since this is also isothermal, **what does the first law say?**  
\[ \Delta U = q + w \]  

isothermal \( \rightarrow \Delta U = 0 \) therefore  
\[ -q = w \]
Notice that the work is just the area under the P-V curve. We will use this a lot.

3. **Isothermal reversible expansion**: Reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. Essentially we are always at equilibrium ($\Delta S = 0$). Thus, $P_{ext}$ must be equal to $P_{gas}$ throughout the expansion.

We can put together a hypothetical example of a piston with a pile of sand on it. Slowly removing sand from piston:
Our work integral is the same, but \( P_{\text{ext}} \) (which = \( P_{\text{gas}} \)) is not constant. So, we can use any of our favorite gas equations to describe \( P \). We’ll use ideal gas right now, but could be Van der Waals or whatever.

\[
w = - \int P_{\text{ext}} \, dV \\
P_{\text{ext}} = \frac{nRT}{V}
\]

So,

\[
w = - \int \frac{nRT}{V} \, dV = -nRT \int \frac{dV}{V} \quad \text{(why can we pull out T? isothermal)}
\]

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

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

Note that reversible path is the maximum amount of expansion work (minimum compression). **Why?** Because reversible by definition utilizes the smallest possible pressure to induce change in volume. If we were irreversible, then \( P_{\text{ext}} \) would be at the final value for the entire expansion \( \Rightarrow P_{\text{ext-irreversible}} < P_{\text{ext-reversible}} \) at all points except the very end.

Notice also that doubling the volume at low temperature (or with few molecules present) is less work than doubling the volume at high temperature (or with many molecules present). Remember that these items came from \( P_{\text{ext}} \) – so higher \( T \) or \( n \), means that \( P_{\text{ext}} \) has to be greater to ensure reversibility.

4. **Reversible adiabatic expansion:**

Remember isothermal was \( \Delta T = 0 \) **For adiabatic what is zero?**

heat: \( q = 0 \)

Adiabatic gives less work than isothermal. We will show in a second that \( T \) drops as the volume increases – thus \( P \) drops even more than in the isothermal case.

**What does the first law let us say about an adiabatic expansion?** \( \Delta U = w \)

So, then \( w = \Delta U = \int_{T_1}^{T_2} C_v dT \)

If \( C_v \) is constant (**for what gas?** Ideal) must have no vibration and no distance-dependent interactions \( \Rightarrow \) Ideal monatomic gas.

Then \( w = C_v \Delta T \)

During expansion, work is done on the surroundings \( \Rightarrow w < 0 \ldots \Delta T < 0 \)

This is our proof that adiabatic reversible is less work than isothermal reversible.
Ok, back to looking at work
\[ dw = \bar{C}_v dT = -p_{\text{ext}} dV \]
for reversible expansion we can say \( p_{\text{ext}} = p_{\text{gas}} \)
\[ \bar{C}_v dT = -p_{\text{gas}} dV \]
for an ideal gas (notice \( C_v \) bar means per mole)
\[ \bar{C}_v dT = -\frac{RT}{V} dV \]

Again, assume \( C_v \) is constant
\[
\frac{\bar{C}_v}{R} \ln \left( \frac{T_2}{T_1} \right) = \ln \left( \frac{V_2}{V_1} \right)
\]
\[
\frac{\bar{C}_v}{R} \ln \left( \frac{T_2}{T_1} \right) = \ln \left( \frac{V_1}{V_2} \right)
\]
\[
z \ln \left( \frac{T_2}{T_1} \right) = \ln \left( \frac{V_1}{V_2} \right)
\]
\[
\left( \frac{T_2}{T_1} \right)^z = \frac{V_1}{V_2}
\]
\[
V_2 T_2^z = V_1 T_1^z
\]
Recall this is for an adiabatic expansion

We haven’t gotten here yet, but trust me that \( C_p - C_v = R \)

You can/should work this out for yourselves... this leads to
\[ P_1 V_1^\gamma = P_2 V_2^\gamma \]
where \( \gamma = C_p / C_v \)

for an ideal monatomic gas \( \gamma = \frac{5R}{2} \)

Even for real gasses \( \gamma \) always \( > 1 \)

These lines of constant \( PV^\gamma \) are called **adiabats**. \( P \propto 1/V^\gamma \)
Recall that lines of constant \( PV \) are called **isotherms** \( P \propto 1/V \) (**Boyle’s law**)
(Show the \( P \) vs. \( V \) plot again)

So, the pressure drops more steeply in an adiabatic expansion. This is because during an isothermal expansion, energy flows into the system to maintain the constant temperature. This keeps the pressure up higher than an adiabatic expansion.