Chapter 36

36 Adiabatic Processes and 2nd Law 2.3.6, 2.4.1

Last lecture we found a way to find Q for solids and liquids, $Q = Mc\Delta T$ or $Q = nC\Delta T$. We need to do this for gasses so we can complete our calculations of the terms in the first law of thermodynamics. We will take on this task in this lecture.

Fundamental Concepts

1. There are four special processes and three of them are isochoric, isobaric, and isothermal and the last one is adiabatic

2. The ratio of the molar specific heats is $\gamma = C_P/C_V$

3. The change in internal energy can be expressed as $\Delta E_{int} = nC_V\Delta T$

4. For adiabatic processes we have two new equations $P_iV_i^{\gamma} = P_fV_f^{\gamma}$ and $T_fV_f^{\gamma-1} = T_iV_i^{\gamma-1}$

5. For insolation the power transferred through the insolation material is given by $\mathcal{P} = \frac{Q}{\Delta t} = \frac{A(T_h - T_c)}{\sum_i R_i}$

6. The power transferred by radiation is given by $\mathcal{P} = \frac{Q}{\Delta t} = \sigma A e T^4$

- Doing work on a system can change the system's temperature. This is called the mechanical equivalent of heat.

- There is a sign convention for energy transfer. If energy leaves it is negative, if it comes into the system it is positive.

- In thermodynamics, we try to find ΔE_{int}, Q, and w for a process. We use the ideal gas law and the first law of thermodynamics to do this.

- We have special processes for which it is easy to find ΔE_{int}, Q, and w

- We are still missing something.

36.1   Constant Q Processes

We found that for isochoric processes there was no work done. And in our first law equation

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

the work is half the equation. That made $\Delta E_{int} = Q$. But could we find a process where Q is zero? Then

$$\Delta E_{int} = w$$

We call a process where $Q = 0$ *adiabatic*.

It might see like we are home free, $Q = 0$! We don't need our molar specific heat equations for an adiabatic process either.

But we don't yet know how to find w for an adiabatic process, and therefor we don't know ΔE_{int}. We need to fix this problem. We could do this by finding an expression for the pressure as a function of volume along the adiabatic path, then use our work equation.
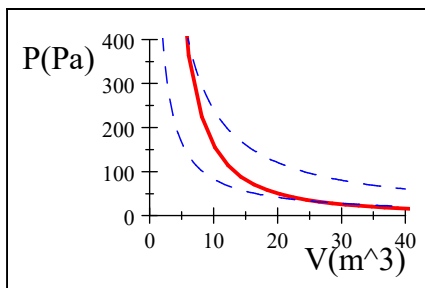
$$w = - \int_{V_i}^{V_f} PdV$$

Since

$$\begin{aligned} \Delta E_{int} &= w \\ &= -\int PdV \end{aligned}$$

this would give us both w and ΔE_{int} . But it is not obvious how to find P as a function of V for this path. We need another strategy.

Let's plot an adiabatic process on a PV diagram to see what it looks like. An adiabatic process goes from one temperature to another temperature, and

$$\Delta E_{int} \propto \Delta T$$

And further remember that ΔE_{int} does not depend on path. So we could find ΔE_{int} for an adiabatic path, and we could find ΔE_{int} for a isochoric path, and as long as the ΔT was the same for both paths, the ΔE_{int} would be the same as well! Also remember that for an isochoric path there is no work done. So

$$Q_{isochoric} = \Delta E_{int}$$

And we know an equation for $Q_{isochoric}$!

$$Q_{isochoric} = nC_V \Delta T$$

So if we know T_i and T_f, then we could find ΔE_{int} by finding the equivalent $Q_{isochoric}$ for the same two temperatures.

$$\Delta E_{int} = nC_V \Delta T$$

This is tremendous! We have an equation for ΔE_{int}, and $w = \Delta E_{int}$, so with $Q = 0$ we have a complete set.

But it turns out that we can add two more equations to our adiabatic set that will really help.

The first is that relationship between pressures and volumes along an adiabatic path. We now know for adiabatic processes we can say

$$\Delta E_{int} = nC_V \Delta T$$

so long as we start with the same T_i and end with the same T_f. A very small change in the internal energy would be

$$dE = nC_V dT$$

Now for our adiabatic process we previously noted that there is no energy transfer by heat done, so

$$\begin{aligned} \Delta E_{int} &= 0 + w \\ &= \int P dV \end{aligned}$$

Then a very small amount of internal energy change, dE_{int} would be

$$dE_{int} = -P dV$$

Let's set these two expressions for dE_{int} equal to each other.

$$-P dV = nC_V dT$$

or

$$-\frac{P dV}{nC_V} = dT$$

Now we know the idea gas law

$$PV = nRT$$

if we take a total differential for a sample of n moles of a gas

$$PdV + VdP = nRdT$$

we can substitute in our expression we have for an adiabatic process for dT

$$PdV + VdP = -nR\frac{PdV}{nC_V}$$

or

$$PdV + VdP = -R\frac{PdV}{C_V}$$

We can use our relationship between C_V and C_P that we found earlier

$$C_V = C_P - R$$

so

$$R = C_P - C_V$$

and let's substitute this in for our R in our total differential equation

$$PdV + VdP = -\frac{C_P - C_V}{C_V}PdV$$

or

$$PdV + VdP = \frac{C_V - C_P}{C_V}PdV$$

Now let's divide through by PV. It's not apparent that this will help, but it does so

$$\frac{PdV}{PV} + \frac{VdP}{PV} = \frac{C_V - C_P}{C_V}\frac{PdV}{PV}$$

and canceling the extra V's and P's gives

$$\frac{dV}{V} + \frac{dP}{P} = \frac{C_V - C_P}{C_V}\frac{dV}{V}$$

rearranging terms gives

$$\frac{dP}{P} = \left(\frac{C_V - C_P}{C_V} - 1\right)\frac{dV}{V}$$

Lets get a common denominator

$$\frac{dP}{P} = \left(\frac{C_V - C_P}{C_V} - \frac{C_V}{C_V}\right)\frac{dV}{V}$$
$$\frac{dP}{P} = \left(-\frac{C_P}{C_V}\right)\frac{dV}{V}$$

Lets define a new quantity

$$\gamma = \frac{C_P}{C_V} \tag{36.1}$$

so we have

$$\frac{dP}{P} = -\gamma \frac{dV}{V}$$

Which is exciting. We are just down to P's and V's and a gamma. We may be able to get an expression of P as a function of V yet! We can integrate this last equation

$$\int \frac{dP}{P} = -\gamma \int \frac{dV}{V}$$
$$\ln(P) + \zeta_P = -\gamma \ln(V) + \zeta_V$$

where ζ_P and ζ_V are the constants of integration. We can write this as

$$\ln(P) + \gamma \ln(V) = -\zeta_P + \zeta_V$$
$$= \zeta$$

where $\zeta = \zeta_V - \zeta_P$ is a constant. And now we need to remember a few things about logs.

$$a \ln b = \ln b^a$$

so we can write our equation as

$$\ln(P) + \ln(V^\gamma) = \zeta$$

and

$$\ln a + \ln b = \ln(ab)$$

so our equation becomes just

$$\ln(PV^\gamma) = \zeta$$

or we can exponentiate both sides

$$PV^\gamma = e^\zeta \tag{36.2}$$

where e^ζ is still just a constant.

Note that we have done what we set out to do (sort of). We have an expression of how P varies with V.

$$P = \frac{e^\zeta}{V^\gamma}$$

We could put this into our work equation and integrate to find the work done in an adiabatic process!

$$\Delta E_{int} = w$$
$$= -\int \frac{e^\zeta}{V^\gamma} dV$$

But also note that we have a great conservation equation for an adiabatic process.

$$PV^\gamma = \text{constant}$$

or

$$P_i V_i^\gamma = P_f V_f^\gamma \tag{36.3}$$

and we know that conservation equations come in very handy in solving problems! Let's add this last equation to our set of equations for adiabatic processes.

We can get a second equation for adiabatic processes relating the volume and temperature. If we know an initial state

$$P_i V_i = nRT_i$$

we can use our adiabatic conservation equation from above to write

$$P_f V_f^\gamma = P_i V_i^\gamma$$

we can solve the ideal gas law for P_i and

$$P_i = \frac{nRT_i}{V_i}$$

and use this in our equation

$$\frac{nRT_f}{V_f} V_f^\gamma = \frac{nRT_i}{V_i} V_i^\gamma$$

to yield

$$\frac{T_f}{V_f} V_f^\gamma = \frac{T_i}{V_i} V_i^\gamma$$

or

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1} \tag{36.4}$$

This is another conservation equation for adiabatic processes! We will add this to our equation set for adiabatic processes

These equations are great shortcuts for problem solving *but remember they are only valid for adiabatic processes!*

Notice that we never did complete the integral for work

$$\Delta E_{int} = w = -\int \frac{e^\zeta}{V^\gamma} dV$$

We totally could at this point, but we already know the answer to be

$$\Delta E_{int} = nC_V \Delta T$$

where the ΔT is the same as it would be for our actual adiabatic process. Since we know this and it is easy to calculate, we won't often do the integral

We still need to find γ for our adiabatic processes. We need the ratio of C_P to C_V or γ. We now know that

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

$$C_P = \frac{5}{2}R$$

and we may take the ratio of these values

$$\begin{aligned}
\gamma &= \frac{C_P}{C_V} \\
&= \frac{\frac{5}{2}R}{\frac{3}{2}R} \\
&= \frac{5}{3}
\end{aligned}$$

This works well for monotonic gasses, but fails badly for more complex gasses. So we see our ideal gas formulation starts to break down with more complex gasses at this point. To go farther, we would need to include the rotational and vibrational energy of the molecules. Still, we have come a long ways with our simple ideal gas assumptions!

Note that for solids and liquids ΔV is very small so very little work is done. This means that $C_P \approx C_V$ which is why we we could get away with only one value for the molar heat capacity in the tables for solids and liquids.

36.1.1 Path Dependence

We should do a problem that shows the path dependence of thermodynamics work. Notice that how we compress the gas (quickly vs. slowly, etc.) makes a difference on our PV diagram. For example, quick actions would not let energy leave by heat, so temperature would rise. Slow actions would allow enough time for energy to leave, allowing the temperature to stay the same. So when we say there is a "path dependence" for thermodynamic work, it is equivalent to saying we have different amounts of work for "different paths" on a PV-diagram. The PV-diagram shows the different physical paths as different lines on the graph. Here is an example.

Suppose we change 1 mol of an ideal gas from one state to another by two different paths. The two paths are shown in the next figure.
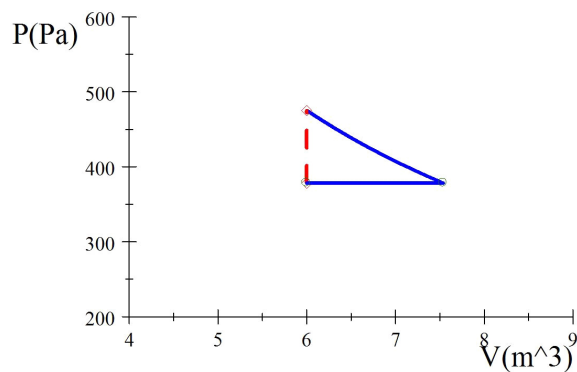
We recognize the blue path as a combination of an isobaric and an isothermal process. So for the blue path, the work done will be a combination of

$$
\begin{aligned}
w_{isobaric} &= -P\left(V_f - V_i\right) \\
w_{isothermal} &= nRT\left[\ln\frac{V_i}{V_f}\right]
\end{aligned}
$$

Then

$$
\begin{aligned}
w_{blue} &= -P\left(V_f - V_i\right) + nRT\left[\ln\frac{V_i}{V_f}\right] \\
&= -378.29\,\text{Pa}\left(7.\,538\,4\,\text{m}^3 - 6\,\text{m}^3\right) \\
&\quad + (1)\left(8.314\frac{\text{J}}{\text{mol K}}\right)(343\,\text{K})\left[\ln\frac{7.\,538\,4\,\text{m}^3}{6\,\text{m}^3}\right] \\
&= 650.\,9\,\text{J}
\end{aligned}
$$

But the red path is an isovolumetric path. We know that for isovolumetric paths the work is zero!

$$
\begin{aligned}
w_{red} &= -\int_{V_1}^{V_2} PdV \\
&= 0
\end{aligned}
$$

and we can see that zero is very different than 651 J! Indeed the work for each PV-diagram path is different. But why?

The red path is what we would get if we put a sealed strong container in a fire. The fire would provide energy to the gas in the container by heat. But the strong walls of the container would keep the gas from expanding. The pressure would rise and the temperature as well. But for the blue path we envision a movable piston in a cylinder of gas. when the fire adds energy by heat, the piston rises, keeping the pressure the same. The temperature does go up. Then we remove the fire, and slowly compress the gas back to its original volume. By doing this slowly the work we do adds a little bit of energy to the gas, but the energy can leave by heat, so the temperature of the gas stays the same.

Note that these are really different processes! So it is no wonder that the internal work done is different. And we see all of this with our PV-diagram!

36.2   Irreversibility

We should ask, are our special processes reversible? We found that for a free expansion the process was not reversible.
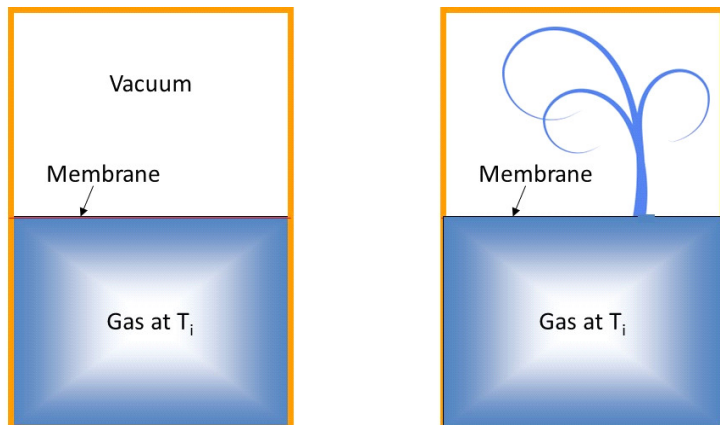
But how about for our special processes: It would make our math easier if they were reversible.

For an isochoric process we know $w_{int} = 0$, $Q = nC_V\Delta T$, $\Delta E_{int} = nC_V\Delta T$. It seems like we can change the pressure of a gas, say by transferring energy by heat, and let the temperature rise, but then cool the cylinder of gas back to the same pressure all without changing the volume. It seems like this would be doable.

For an isobaric process we know $w_{int} = -P\Delta V$, $Q = nC_P\Delta T$, $\Delta E_{int} = nC_P\Delta T - P\Delta V$. It seems like we could make a cylinder with a free floating position that could go up or down. We could transfer energy by heat and let the volume increase. But then transfer energy back out of the cylinder to restore it to the same pressure. This seems reversible.

For an isothermal process $w = -nRT\left[\ln\dfrac{V_f}{V_i}\right]$, $Q = -w$, $\Delta E_{int} = 0$. Could we do work on a cylinder of gas that is in an ice water bath and transfer energy out by heat such that the temperature stays the same, then pull the piston back out allowing energy to transfer back in by heat, still keeping the temperature the same? This also seems possible.

Finally, for an adiabatic process we now know that $w = \Delta E_{int}$, $Q = 0$ and $\Delta E_{int} = nC_v\Delta t$ for an equivalent process. So we insolate our cylinder and do some work. That increases the internal energy (and the temperature) but we pull the piston back out and the internal energy reverts back. These all seem like reversible processes. But notice that in each case, though the cylinder contents came back to the same state, the surroundings would not be the same. It each case energy was transferred either work or by heat. And the surroundings had to supply that work or energy transfer by heat. And we expect that in energy transfer by heat that not only was our cylinder affected by a stove or hotplate and the air in the room would also have a larger temperature. In the case of work our diligent coresearcher that kept pushing and pulling pistons is now tired. The surroundings are different. Causing a change in the surroundings is something we need to think about, and it gives us our first version of the *Second*

Law of Thermodynamics.

36.3   The Second Law of Thermodynamics

We did a lot with our first law of thermodynamics (using our ideal gas law). But there is a second law of thermodynamics. It is a little harder to state in a nice equation. So we are going to build up to it a little at a time. Our first version is due to a researcher called Clausius, so it is called the Claussius statement of the Second Law of Thermodynamics.

It is impossible to make a cyclical machine that transfers energy spontaneously from a colder object to a hotter object

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This seems obvious. Refrigerators have to be plugged in, so do air conditioners. They require an input of energy to run. But this is just what we have been discussing. for a refrigerator or an air conditioner to work the surroundings have to change. Energy in the form of electricity has to be supplied. And that not only changes the surroundings it also changes our budget. In our next lectures, we will form more mathematical statements of the second law.