Chapter 2

The First Law of Thermodynamics

- This is where I like to start (along with the 2nd Law), which is why I did the work=heat and heat=work demos.

- The reason I like to start here is because it explains why we do thermo: Newton's Laws, Maxwell's equations, etc. give us work, but we need thermo to understand heat and heat=work conversions.

- The 1st Law (and the 2nd) can be stated in terms of a "perpetual motion" machine: "you can't get motion w/o energy input" (1st Law) and "you can't get heat to convert 100% into work (e.g., motion)" (2nd Law).

- The 1st Law is easy to write for closed systems: $dU = dQ + dW$ where $dU$ is the energy exchanged with the surroundings in a time dt and $dQ$ and $dW$ are components of that exchange. $dQ$ is the component that's exchanged due to a temperature difference as the "driving force," and $dW$ is due to any other driving force (e.g., mechanical, etc.).

- For open systems we write $dU = dQ + dW + dU_{\text{matter}}$, where $dU_{\text{matter}} = \sum \left( \frac{\partial U}{\partial N_i} \right) dN_i$ (p.62), $N_1, N_2, \ldots, N_i, \ldots, N_n$ are the number of moles for each type of particle.

- So basically there are 3 ways to exchange energy (we already knew this from our definitions of various systems): exchange driven by temperature difference, exchange linked to matter (driven, as we'll see, by chemical potential), and exchange of any other type, which we call "work."
- Two things from Chp 1 we glossed over: Kelvin scale, 0th law.
  The Kelvin scale starts at 273.15°C and 1 Kelvin = 1°C
  The Zeroth law of Thermodynamics says: if A⇔B, B⇔C then A⇔C
  (where ⇔ means in thermal equilibrium)

- With our new understanding of dQ, we can now define heat capacity: \( C = \frac{dQ}{dT} \) i.e., the ratio of heat input to resulting temp. increase.

- We saw heat capacity while considering "equipartition":
  Now we have a better expression for it.

- We distinguish \( C_p \) (const. pressure) from \( C_v \) (const. volume).

- We do calorimetry to find dQ, but first we need to know C in ideal gas.

- Let's talk more about work. We know \( W = F \cdot S \) and \( dW = F \cdot ds \), what about work done on (cyclic) a gas? \( dW = P \cdot dV \) by gas.
  So for work done on a gas, \( dW = -pdV \).

- Let's look at a real example of "pV" work: \( h \) increases

- In this case, work = \( \int_{h_1}^{h_2} dW = -mg(h_2-h_1) = -p_a(v_2-v_1) \).
  IF \( p_a = 0 \), work = 0.

- Notice how this is the same as the area in the p-V graph!

- For a reversible change in an ideal gas, \( \int_{V_1}^{V_2} pV = \int_{V_1}^{V_2} \frac{dNRT}{V} = -NRT \ln \left( \frac{V_2}{V_1} \right) \).
The Relationship between $C_p$ and $C_v$

- Recall $C_p = \left( \frac{\partial Q}{\partial T} \right)_p$ and $C_v = \left( \frac{\partial Q}{\partial T} \right)_v$. $C_v$ is useful, since no $pV$ work can be done, thus $dU = dQ$ and $C_v = \left( \frac{\partial U}{\partial T} \right)_v = \left( \frac{\partial Q}{\partial T} \right)_v$.

- The reason we use "$U$" with $U$ and "$d" with $Q$ is that $U$ is a function of many variables, whereas $dQ$ is just quantifying the change of $U$ due to heat, so it can't be expressed as a function of $P, V, T$ etc.

- Using our partial derivative expression: $dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + dQ_{nr}$.

Now $dW = -pdV$, so $dQ = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + pdV \rightarrow \left[ \rho + \left( \frac{\partial U}{\partial V} \right)_T \right] dV$

Thus $(\frac{\partial Q}{\partial T})_p = \left( \frac{\partial U}{\partial T} \right)_V \frac{dT}{V} + \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \frac{dV}{V} = C_p$. What is $C_p - C_v$?

$\rightarrow \left( \frac{\partial U}{\partial T} \right)_V + \left( p + \left( \frac{\partial U}{\partial V} \right)_T \right) \frac{dV}{V} = p \left( \frac{\partial U}{\partial T} \right)_p = p \left( \frac{\partial NRT}{\partial T} \right)_p = NR$

$s = 0$ for an ideal gas

So, $C_p - C_v = NR$ or $C_p - C_v = R$ for an ideal gas

- We saw that isotherms are pretty easy to handle, what about adiabats?

No heat exchange: $dQ = 0 = dU + pdV = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + pdV$, $C_v N\gamma = \left( \frac{\partial U}{\partial T} \right)_V dT$

So, $C_v N\gamma dT + pdV = 0 = C_v dT + \frac{pT}{V} dV$ (divide by $T + C_v$, $R = C_p - C_v$, so $\frac{dT}{V} + \frac{C_p - C_v}{C_v} dV = 0$ i.e. $\int \frac{dT}{V} + \frac{C_p - C_v}{C_v} dV = 0$, i.e. $T \cdot V^{(\gamma - 1)} = \text{const.}$ (constant))
another time we use the ratio $\frac{CP}{CV} = \gamma$ is for sound propagation, since sound waves cause such fast pressure changes that it's adiabatic.

As we might guess (and as we learned in intro physics) speed of sound = \( \sqrt{\frac{E}{\rho}} \)

\( B \), the "bulk modulus" = \(-V \frac{dP}{dV}\), for adiabatic things = \( \gamma \rho \), since \( \rho = \frac{\text{const}}{V} \)

(note: we get \( \rho = \frac{\text{const}}{V^2} \) from \( TV = \text{const.} \) and \( PV = \text{NRT} \))

Now \( \rho = \frac{\text{NRT}}{V} = \frac{N \cdot M \cdot RT}{V \cdot M} = \frac{\rho RT}{M} \), plugging this in: \( B = \gamma \rho \frac{RT}{M} \)

Plugging in again: speed of sound = \( \sqrt{\frac{\rho RT}{M}} \), pretty neat!