

## Chapter 2 2.1

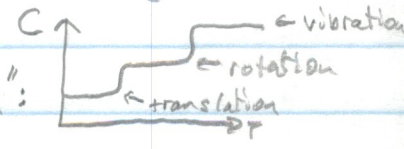
### The First Law of Thermodynamics

- This is where I like to start (along with the 2<sup>nd</sup> Law), which is why I did the work  $\rightarrow$  heat and heat  $\rightarrow$  work demos.
- The reason I like to start here is because it explains why we do thermo: Newton's Laws, Maxwell's eqns, etc. give us work, but we need thermo to understand heat and heat  $\leftrightarrow$  work conversion.
- The 1<sup>st</sup> Law (and the 2<sup>nd</sup>) can be stated in terms of a "perpetual motion" machine: "you can't get motion<sup>(i.e. work)</sup> w/o energy input" (1<sup>st</sup> Law) and "you can't get heat to convert 100% into work (e.g. motion)" (2<sup>nd</sup> Law)
- The 1<sup>st</sup> 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  $\rightarrow dQ$  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  $dU_{\text{matter}} = \sum_k \left( \frac{\partial U}{\partial N_k} \right)_{V, T, N_{i \neq k}} dN_k$  (p. 62),  $N_1, N_2, \dots, N_i, \dots, N_k, \dots$  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, 3<sup>rd</sup> Law: The Kelvin scale starts at  $-273.15^{\circ}\text{C}$  and  $1\text{ Kelvin} = 1^{\circ}\text{C}$
- The Zeroth law of Thermodynamics says "if  $A \leftrightarrow B, B \leftrightarrow C$  then  $A \leftrightarrow C$  (where " $\leftrightarrow$ " means "in thermal equilibrium with")

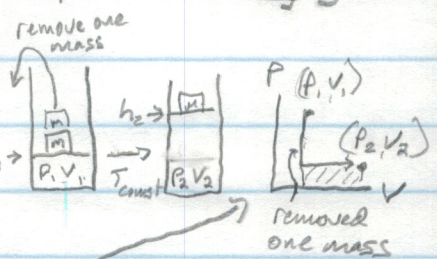
- With our new understanding of  $dQ$ , we can now define heat capacity:  $C = dQ/dT$  i.e. the ratio of heat input to resulting temp. increase

- 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  $C_{\text{calorimeter}}$

- Let's talk more about work. We know  $W = F \cdot s$  and  $dW = F \cdot ds$ , what about work done on (or by) a gas?  $dW = \frac{F}{A} \cdot A ds = p \cdot dV =$  done by gas  
 so for work done on a gas,  $dW = -p dV$

- Let's look at a real example of "pV" work: 

- in this case work =  $\int_{h_1}^{h_2} dW = -mg(h_2 - h_1) = -p_2(V_2 - V_1)$  (if  $p_2 = 0$ , work = 0)

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

- for a reversible change in an ideal gas,  $\int_{V_1}^{V_2} -pdV = \int_{V_1}^{V_2} -\frac{NRT}{V} dV = -NRT \ln\left(\frac{V_2}{V_1}\right)$



## The Relationship between $C_p$ and $C_v$

Recall  $C_p = \left(\frac{\partial Q}{\partial T}\right)_{\text{const } p}$  and  $C_v = \left(\frac{\partial Q}{\partial T}\right)_{\text{const } v}$ .  $C_v$  is useful, since no PV work can be done, thus  $dU = dQ$  and  $C_v = \left(\frac{\partial Q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$

The reason we use "d" 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  $T, V, T$  etc.

Using our partial derivative expression  $\rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \stackrel{\text{1st Law}}{=} dQ + dW$

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

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

$\rightarrow \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v = p \left(\frac{\partial V}{\partial T}\right)_p = p \left(\frac{\partial \frac{NR T}{p}}{\partial T}\right)_p = NR$   
 $\rightarrow = 0$  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:  $dQ = 0 = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$ ,  $C_v \cdot N = \left(\frac{\partial U}{\partial T}\right)_v$   
zero, for an ideal gas

so,  $C_v N dT + pdV = 0 = C_v dT + \frac{RT}{V} dV$ , divide by  $T + C_v$ ,  $R = C_p - C_v$ , so

$\frac{dT}{T} + \frac{C_p - C_v}{C_v} \frac{dV}{V} = 0$  i.e.  $\int \frac{dT}{T} + \left(\frac{C_p}{C_v} - 1\right) \int \frac{dV}{V} = \int (\text{zero}) d?$ , i.e.  $T \cdot V^{(\frac{C_p}{C_v} - 1)} = \text{const.}$



another time we use the ratio  $\frac{C_p}{C_v} \equiv \gamma$  is for sound propagation, since sound waves cause such fast pressure changes that it's adiabatic. 2.4

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

$B$ , the "bulk modulus", =  $-V \frac{dP}{dV}$ , for adiabatic things =  $\gamma P$ , since  $P = \frac{\text{const.}}{V^\gamma}$

*more "springy" means more pressure change as volume changes*

*springiness of medium*

*density of medium*

(note: we get  $P = \frac{\text{const.}}{V^\gamma}$  from  $TV^{(\gamma-1)} = \text{const.}$  and  $PV = NRT$ )

Now  $\rho = \frac{NRT}{V} = \frac{N \cdot M}{V} \frac{RT}{M} = \overset{\text{density "rho"}}{\rho} \frac{RT}{M}$ , plugging this in:  $B = \gamma \rho \frac{RT}{M}$

Plugging in again: speed of sound =  $\sqrt{\frac{\gamma RT}{M}}$ , pretty neat!