

Lecture #1
Thermo

Calton Ch 1

→ Although we don't often think of it, we know that atoms exist. And there are lots of them. Like a lot. In Chemistry we learn about a mol. What is a mol?

- It's a big number. 6.022×10^{23}
- 12g of carbon has that many atoms
- the graphite in my pencil weighs about 12 grams
- now imagine all of these particles are interacting. Not hard to do because they are.



• We're not sure what that interaction is yet

(I haven't told you) but I know it depends on distance, has a push back at small r, a pull @ large r, a minimum and a breaking point

$$F = ma \quad W = \int \vec{F} \cdot d\vec{l}$$

↗ do you know this?

1-3

$$\ddot{x} + \frac{k}{m}(x - x_0) = 0$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$\ddot{x} + \omega^2(x - x_0) = 0$$

$$x(t) = C_1 \cos(\omega t) + C_2 \sin(\omega t)$$

$$= A \cos(\omega t - \phi)$$

$$A = \sqrt{C_1^2 + C_2^2}, \tan \phi = (C_2 / C_1)$$

I can even get an average position

Okay now I'll make it harder, add 2 normal modes, etc...

What about when force is different (non harmonic?) when there are 10^{23} ... harder

Computer

$$x_0 \rightarrow \quad x_0^0 = 1, v_0^0 = 0.1$$

$$v_0 \downarrow \quad x_1^0 = 3, v_1^0 = 0.2$$

or

for $i \neq j$

$$f_i^0 = -k_{ij} (\vec{x}_i^0 - \vec{x}_j^0)$$

for i : $F = ma$

figure out acceleration
use rel, update, calc, iterate

? ?

Molecular dynamics

1-5

For a galaxy, it could mean entire solar systems

For an explosion, the timescale could be a nanosecond compared to 10,000 years for decomposition

How can we tell?



conformation A, length A



conformation B, length B



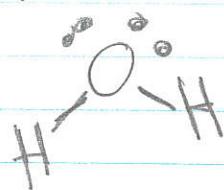
vs



$$l_m \gg \Delta l$$

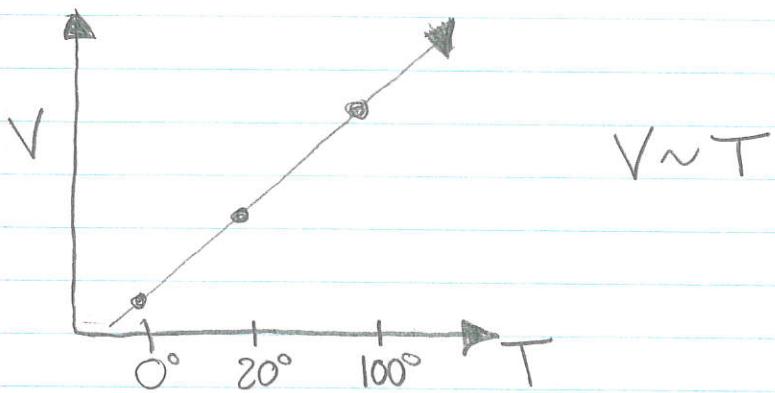


fluctuations in the total length



OH stretch frequency

I-7

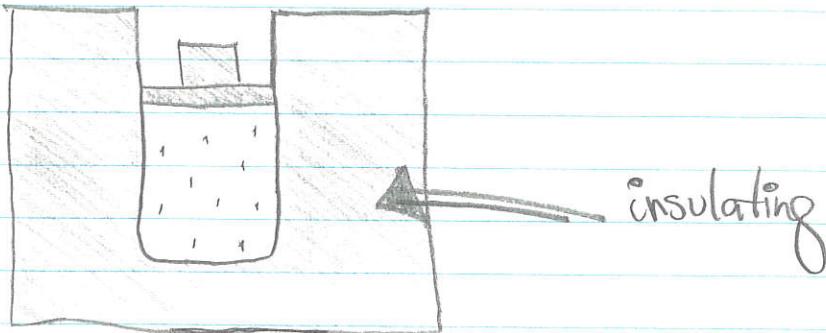


$$V \sim T$$

$$PV \sim MT$$

$$PV = NRT \leftarrow \text{ideal gas law}$$

We can imagine other experiments



$$PV^{5/3} = \text{const}$$

End of Lecture
#1



Do I have to
do an experiment
every time?

\Rightarrow pencil lead

\Rightarrow predict or report?

Thermodynamics

Lecture #2

- Last lecture we discussed the need for TD to treat macroscopic systems
- We said that macroscopic means large compared to the characteristic time and length scale of the problem. Macroscopic measurements represent averaged quantities. If you notice that fluctuations in your system result in noticeable changes in these measurements, chances are you are not in the "thermodynamic limit".
- There is an additional "requirement" to come
- We also discussed different experiments which can be performed on a simple system

By simple system, I mean it meets the following criteria

- homogeneous
- isotropic (if's design, not just composition)
- uncharged
- no chemical rxn's

If a system meets these criteria, then symmetries are present which correspond to the following variables being relevant thermodynamically

- Volume, V
- mass & composition, N
- internal energy, U

~~What is different about these experiments?~~

~~what we hold constant or change
what we're measuring~~

"Walls" * not literally a wall (necessarily)
but rather a constraint

Different types of constraints or walls

rigid	\leftrightarrow	$dV = 0$, measure volume
moveable	\leftrightarrow	$dV \neq 0$, mechanical work
impermeable	\leftrightarrow	$dN = 0$, measure chemical composition
permeable	\leftrightarrow	$dN \neq 0$, alter composition
adiabatic	\leftrightarrow	$dQ = 0$, suppress heat transfer
diathermal	\leftrightarrow	$dQ \neq 0$, allow for it

e.g.

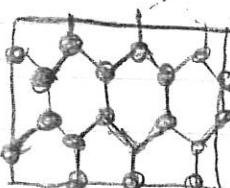
rigid



moveable



permeable



CO_2 vs O_2 vs N_2

adiabatic styrofoam, house insulation

diathermal metal container

Walls are about Measurements & constraints

Some of these walls are relatively easy to understand as they are familiar from our day-to-day existence. The walls in this room are rigid and impermeable. I can't walk through or move them. A face mask (it's cold out) lets air through but keeps my face warm. Aspects of this are tricky though, because they involve non-obvious quantities like energy.

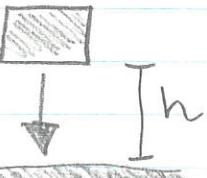
What is energy?

"It is important to realize that, in physics today, we have no knowledge what energy is. We do not have a picture that energy comes in little blobs of a definite amount"

- R.P. Feynman

→ So what can we say? ←

There is a number which we can calculate according to a certain rule, and as nature goes about its miracle of changes this number will not change.



$$F = -mg$$

$$\epsilon_1 = -mgh$$

$$\epsilon_2 = \frac{1}{2}mv^2$$

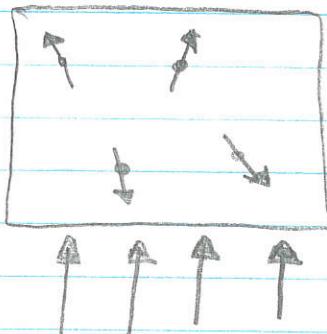
As the object falls, we know that $\epsilon_1 \rightarrow \epsilon_2$ such that their sum is constant.

2-7

The ability to alter the energy of a system through the addition or removal of heat is what sets TD apart from any other theory

Note that for "non simple systems", it is possible to change the internal energy by additional means

e.g. magnetic work



$$dU = dQ + dW + B_0 dM$$

field

Similarly, if we relax the constraint on mol number, we can do chemical work

$$dU = dQ + dW + \mu dN$$

chemical potential

And of course both at the same time

$$dU = dQ + dW + \mu dN + B_0 dM$$

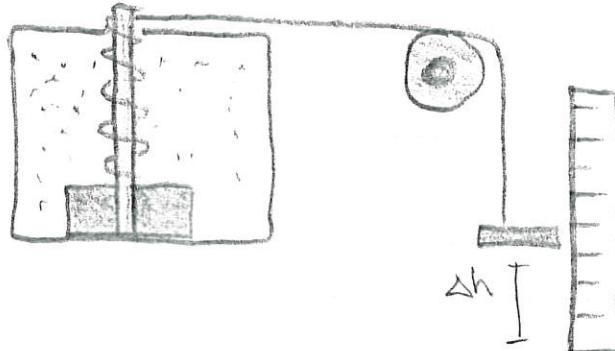
forms of "work"
 heat

Clearly this process was done by something other than work. Indeed work done was 0 b/c $\Delta V = 0$

But I've told you heat transfer can't be directly measured or calculated. So what can we say about the final energy?

It turns out we can get to the same ~~End~~
~~thermodynamic state by mechanical means alone & lecture~~

V, P_f, T_f, U_f (see next lecture)



By measuring the Δ height of the weight we know how much mechanical energy is transferred into the motion of the paddle wheel. It turns around and around, bumping into the atoms of the gas. This continues until it eventually comes to a halt. No heat has been transferred yet we are at the same spot. This demonstrates the equivalence of heat and work.

Now, suppose we wish to cool the system back down. Well, we just turn the paddle

3-1

Last lecture: - We discussed different ways to change the internal energy of a system

- we divided these into two broad categories: Heat and "Work"

"Work" can have many meanings including the familiar mechanical work as well as other types like chemical, magnetic & so on

- now we are restricting ourselves to simple systems at constant mol number - so our expression for changes to the internal energy is

$$dU = dQ + dW$$

heat work

- we also noted that heat cannot be directly measured or calculated

- I left you with a puzzle

- The connection between heat & work

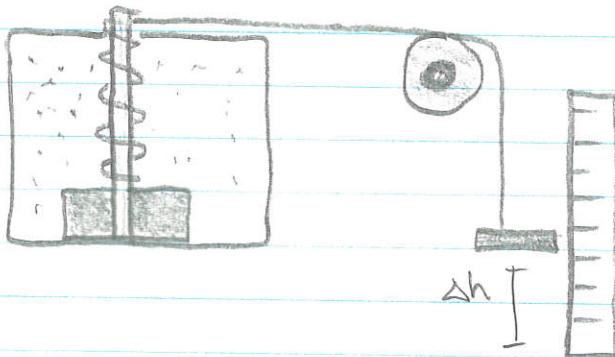
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Lecture 2

It turns out we can get to the same thermodynamic state by mechanical means alone ~~of lecture~~

$$V, P_f, T_f, U_f$$

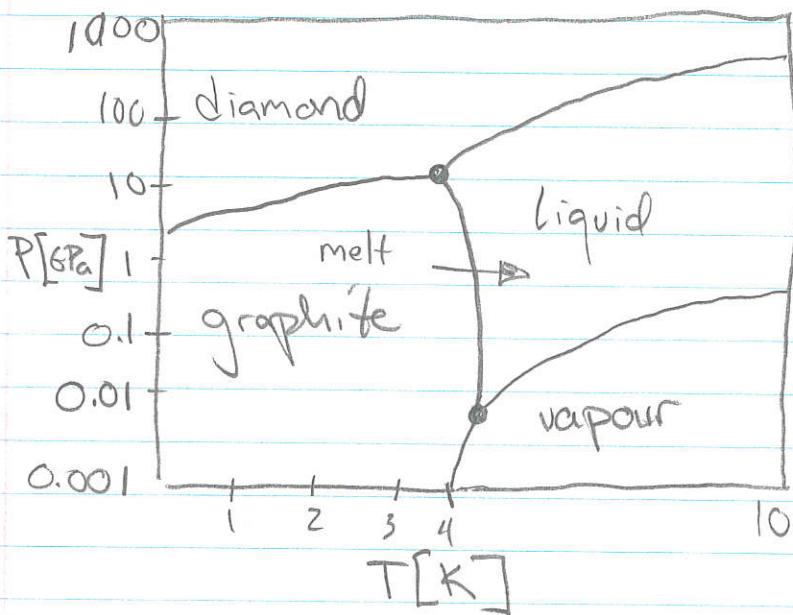


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④ Diamond

→ Depends. The diamond ring you've always wanted is not at equilibrium, but if you find yourself at $T=1000\text{ K}$ and $P=10\text{ GPa}$, then it is



The above is called an "equilibrium phase diagram". It is a record (or prediction) of the equilibrium state of matter for a given set of thermodynamic conditions.

So if we take the diamond example, we can check. Clearly we are in the graphite portion of the P (t).

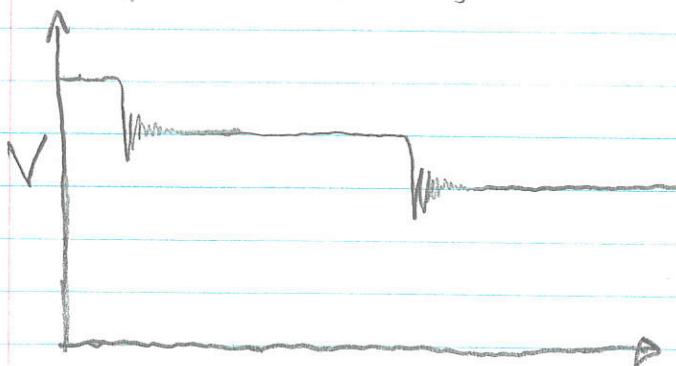
Non-equilibrium phases may be very stable in absolute terms. Strictly speaking a diamond could in principle experience a fluctuation in enough kick to transform (can be done w a spark). There is an activation energy

3-6

We introduce the notion of a quasi-static process

A quasi-static process is one which occurs slowly compared to the characteristic timescale of relaxations in the system. Such a process will take the system through a series of equilibrium states in the limit of $dt \rightarrow 0$, which means total time $\rightarrow \infty$

In practice, we just need $dt/\tau \sim 0$



What would qualify?

Consider a car engine: 6,000 rpm

That means 100 rps, which means 1 revolution takes $0.01 \text{ s} \approx 100 \text{ ms}$

A density disturbance will travel across the cylinder at the speed of sound

$$v_s \sim 500 \text{ m/s}$$

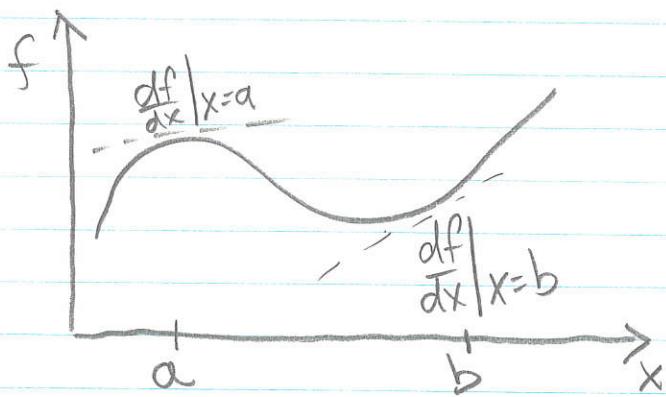
$$L \sim 20 \text{ cm}$$

$$t_{\text{rel}} \sim \frac{L}{v_s} = 0.4 \text{ ms}$$



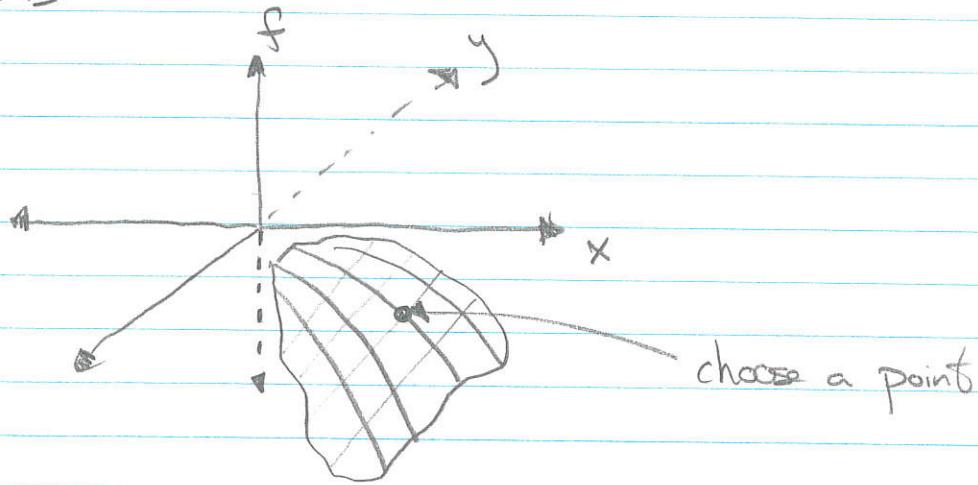
two orders of magnitude

3-8



The value of the slope (derivative) depends on where you evaluate it

In 2D



$$f = f(x, y)$$

$\frac{\partial f}{\partial x} \Big|_y$ = partial derivative of f wrt x
holding y constant

we hold a 1D variable const
(rather than just a 0D value)

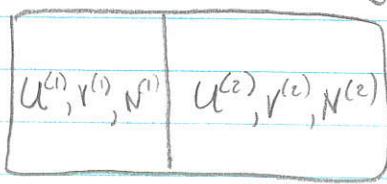
$\frac{\partial f}{\partial y} \Big|_x$ = partial derivative of f wrt y
holding x const

Last lecture: We discussed the concepts of equilibrium states and quasi-static processes

Recall an equilibrium state is independent of the past and does not vary with time. A quasi-static process is one which occurs slowly compared to the characteristic timescale of fundamental relaxations, so the system evolves through a set of nearly equilibrium states.

We would like to understand and predict equilibrium conditions.

Consider the following



rigid, adiabatic, impermeable walls
i.e. two closed systems

U, V, N are extensive, so

$$U = U^{(1)} + U^{(2)}$$

$$V = V^{(1)} + V^{(2)}$$

$$N = N^{(1)} + N^{(2)}$$

If we remove this internal constraint of this composite system, what happens to $U^{(1)}, V^{(1)}, N^{(1)}$?

(we could poke a hole, let the piston go, etc)

We expect a new equilibrium, i.e. a redistribution of energy, volume, or mass (or all three)

Now we have done something interesting. We originally talked about macroscopic variables which we are familiar with from previous experience energy, volume, mass.

We then said we were interested in equilibrium conditions and designed a function to record them.

But now we arrive at a situation where suddenly there is a new parameter on equal footing with the others.

$$U = U(S, V, N)$$

what is this?

Answer: entropy. You have likely heard of the entropy at some point. "It is a measure of disorder". Sound familiar? Now we see it relates to equilibrium too.

For now let's hold off on a full interpretation and let's see how these "fundamental relations" behave.

(Note: The fundamental relation contains all thermodynamic information that can be obtained, calculated, or observed).

Let's take the fundamental relation in the energy representation

$$U = U(S, V, N)$$

Write down in differential form

Comparing, we see

$$\boxed{dQ = TdS}$$

What about if instead we focus on the entropy representation. Both contain the same information, so formally it does not matter.

$$S = S(U, V, N)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

here

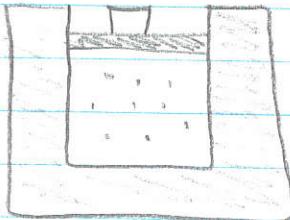
$$\left.\begin{aligned} \left(\frac{\partial S}{\partial U}\right)_{V,N} &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial V}\right)_{U,N} &= \frac{P}{T} \\ \left(\frac{\partial S}{\partial N}\right)_{U,V} &= -\frac{\mu}{T} \end{aligned}\right\} \text{commit these to memory}$$

So rewrite

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN} \quad \text{Know how to derive}$$

We now have expression for changes in both the energy and entropy representation.

In your assignment you will work in a system we discussed in the first lecture



Ideal gas, adiabatic, impermeable walls in a moveable piston

You will see that for this set of walls, $P(V)$ follows $P^3 V^5 = \text{const}$

Here the 3:5 depend on the details of the gas (monoatomic? diatomic, etc?)

We also had the familiar result of $PV = NRT$

Now I'm going to add another relation to the mix:

$$U = \frac{3}{2} NRT$$

← you may or may not have seen this before
(it can be derived from classical kinetic theory)

We now have several relations about macroscopic properties of a gas. None of them are fundamental relations though!
(no entropy)

What can we do with them?

Write $PV = NRT$ as

$$\frac{P}{T} = \frac{N}{V} R$$

4-9

$$ds' = \frac{1}{T} ds' + \frac{P}{T} dv'$$

$$ds' = \frac{3R}{2} \frac{du}{u} + R \frac{dv}{v}$$

↑ ↑
 terms do not depend on one
 another

So integrate separately

$$s' = s_0 + R \ln \left[\left(\frac{u'}{u_0} \right)^{3/2} \left(\frac{v'}{v_0} \right) \right]$$

↗ ↗
 const of integration, necessary for dimensions
 (functions can't have units!)

(u_0, v_0, N_0) is a reference state from which
 we take differences (recall no absolute energy
 meaning)

The more general form, i.e. unconstrained
 mol number is given by

$$S = Ns_0 + NR \ln \left[\left(\frac{u}{u_0} \right)^{3/2} \left(\frac{v}{v_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right]$$

4-11

$$\text{const} = \left(\frac{3}{2} v' P \right)^{3/2} v'$$

$$\text{const} = P^{3/2} v'^{5/2}$$

$$N \cdot \text{const} = P^{3/2} v'^{5/2}$$

$$\text{const}^2 = P^3 v'^5$$

$$\boxed{\text{const} = P v'^{5/3}}$$

← trajectory in PV plane.

Similarly

$$\boxed{\text{const} = P T^{-5/2}}$$

← trajectory in PT plane

Last lecture: We started to look at fundamental relations in both the energy and entropy representation

$$U = U(S, V, N) \Leftarrow \text{FR in energy rep}$$

$$S = S(U, V, N) \Leftarrow \text{FR in entropy rep}$$

We also showed how to express changes e.g.

$$dU = TdS - PdV + \mu dN, \text{ energy rep}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN, \text{ entropy rep}$$

This was accomplished by writing out the full derivative and identifying certain partials

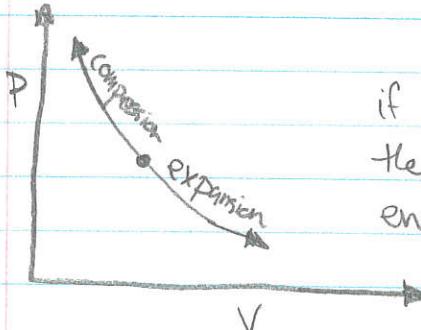
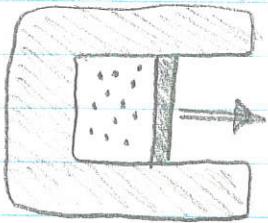
$$\text{e.g. } \left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}, \text{ etc.}$$

Note that the fundamental relation of any system can be written in either rep as each contain all thermodynamic information. Typically you will find that for a given problem one may be a more useful form than another (this happens in QM too, sometimes $\psi(x)$ is less useful or clear than $\psi(k)$)

Finally, we started to work in the FR of the ideal gas to derive the expression of the adiabat,

What does this mean physically?

For this purely mechanical gas (i.e. everything is about kinetic energy, no particle interactions)



if we expand, and do nothing to the number of particles or their kinetic energy, less particles will hit/unit time achieving the same pressure @ lower density requires faster moving or more gas moles

To go horizontally in PV plane, some heat is required (to stay above the adiabat). To go below it, heat must be extracted. For a given initial point, there is one adiabat.

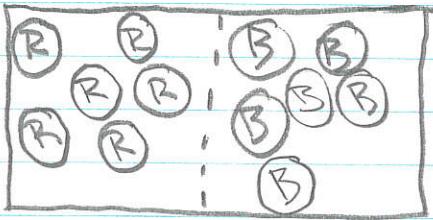
The Laws of Thermodynamics

1st law: The energy of an isolated system is conserved.

To change the energy, we must do work (or allow the system to do it) and add or remove heat

$$dU = dQ + dW$$

When we put in the particles, we are careful to put blue ones on the right and red ones on the left hand side.



For simplicity, we will assume these particles interact like hard spheres (e.g. billiard balls). When not in contact they exert no forces on each other and scatter (collide) elastically. Momentum is conserved.

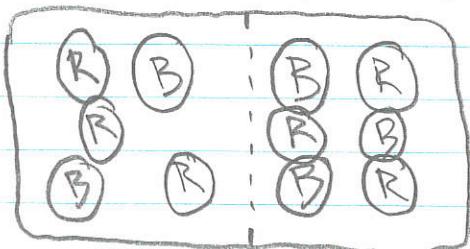
Now, if I let this system evolve w time, what happens?

Nothing!

Okay, what about if there are random initial velocities. They bump into one another.

At the sides $R - R$ & $B - B$ and at the interface, $R - B$ such that some cross the line.

Concievably, if I left for awhile I might come back to find



Ask someone else, which side was initially red?

6-1

Last lecture: We started to discuss the Laws of Thermodynamics. We got through 2:

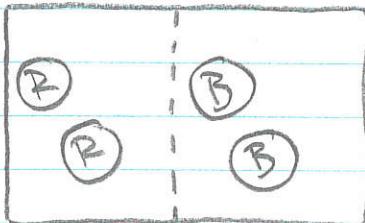
1st: $dU = dQ + dW$, Energy is conserved

2nd: S increases in an isolated system until it reaches equilibrium. At equilibrium, entropy is maximized.

And I left you with a puzzle about particles in a box.

Recall, we noticed unmixed \rightarrow mixed seems reasonable whereas mixed \rightarrow unmixed does not

Collisions & scattering are invariant wrt $t \rightarrow -t$



(we'll think about 4 particles for the moment)

6-2

Let's think about the counting problem we have in front of us.

(restrict to 4 for now)

I have 2 red particles and 2 blue particles. How many ways can I put these particles down where they are fully unmixed?

1	2	3	4	
1	2	3	4	
1	2	3	4	
1	2	3	4	
2	3	4	1	
2	3	4	1	
2	3	4	1	
2	3	4	1	
3	4	1	2	
3	4	1	2	
3	4	1	2	
3	4	1	2	
4	1	2	3	
4	1	2	3	
4	1	2	3	
4	1	2	3	
4	3	1	2	
1	2	4	3	
1	2	4	3	
2	4	1	3	

$$\text{red} = 1, 2$$

$$\text{blue} = 3, 4$$

$$\text{note } 1234 = 4321$$

$$2^N = 2^4 = 16 \text{ options}$$

6 have equal number

8 have 1/3 or 3/1

2 have all to one side

2 are fully unmixed

What is special about equal (or nearly equal) states vs "all-to-the-left" vs "all-to-the-right"? Nothing. There do seem to be more of them however.

This is for a trivial case of 4 particles. What about 10?

$$2^{10} = 1024. \text{ Still only 2 on LHS/RHS.}$$

" " " fully demixed

(6-4)

The nature of the walls prevent several options though

$$\text{so } dS = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}} \right)_{V, N} dU^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}} \right)_{V, N} dU^{(2)}$$

$$dS = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)}$$

since energy is conserved

$$dU^{(1)} + dU^{(2)} = 0$$

$$dU^{(2)} = -dU^{(1)}$$

$$dS = \frac{1}{T^{(1)}} dU^{(2)} - \frac{1}{T^{(2)}} dU^{(1)}$$

$$dS = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)}$$

Recall that an isolated system will tend toward maximum entropy (e.g. at equilibrium)
(2nd Law)

Maximum means no slope, $dS = 0$

$$0 = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)}$$

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}$$

$$\boxed{T^{(1)} = T^{(2)}}$$

@ equilibrium, irrespective of how things got started, temperatures will equalize.

6-6

What about if that side was colder?

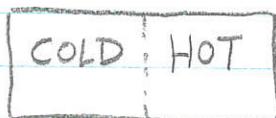
$$T^{(2)} < T^{(1)}$$

$$\left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right] dU^{(1)} > 0$$

$$[-ve] dU^{(1)} > 0$$

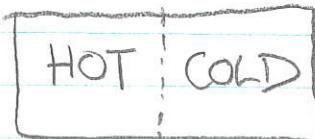
$dU^{(1)}$ is -ve, energy decreases when wall allows

case 1: $T^{(2)} > T^{(1)}$



$dU^{(1)} \uparrow, dU^{(2)} \uparrow$
heat flows ←

case 2: $T^{(2)} < T^{(1)}$



$dU^{(1)} \downarrow, dU^{(2)} \uparrow$
heat flows →

A gradient in temperature leads to heat transfer i.e. conduction

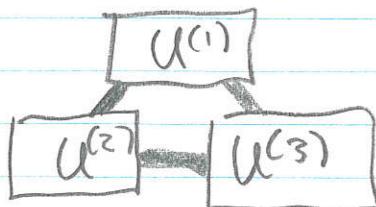
Last lecture: We discussed the 2nd Law and its physical origin - i.e. many more states which are disordered compared to those which are ordered. When there is no preference between them (through interactions) disordered states dominate by sheer numbers.

"Counter examples" do exist: oil and water

Here at the microscopic level there are differences between oil-oil, oil-water, and oil-water interactions.

Another conclusion we arrived at was that thermal equilibrium comes out naturally from the entropy maximum principle. Furthermore, we associated gradients of intensive parameters leads to transport of extensive quantities.

Let's now look @ a similar case



here, like before

$$U = \sum_i U^{(i)}, \quad S = \sum_i S^{(i)}$$

$$dU = \sum_i dU^{(i)}, \quad dS = \sum_i dS^{(i)}$$

Note that we have a problem however

3rd Law: The least clear (at least in terms of what it is).

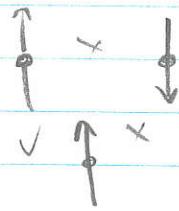
Some people say $S \rightarrow 0$ as $T \rightarrow 0$
 $S = 0$ at $T = 0$
 $\Delta S = 0$ at $T = 0$

So why the confusion?

Originally it was @ $T=0$, $S=0$

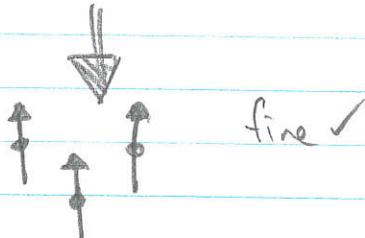
examples include a perfect (i.e. defect free) crystal. When no thermal excitations are possible, by symmetry alone we expect perfect, non-disordered structures.

Some toy models cause a problem though



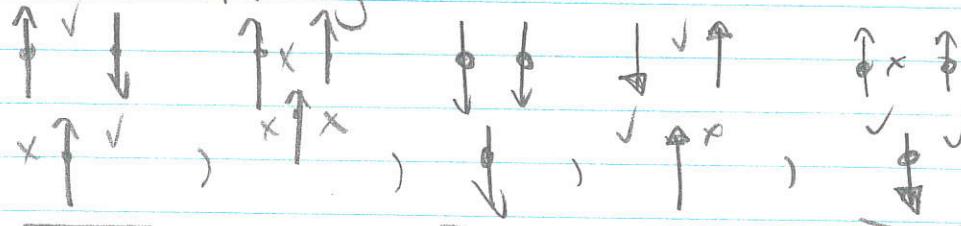
$\uparrow\uparrow$ = good (ferrononet)

$\uparrow\downarrow$ = bad



but when $\uparrow\uparrow$ = bad

$\uparrow\downarrow$ = good



lowest energy

Let's consider the consequence of another rule (postulate we have imposed)

Fundamental relations are homogenous 1st order functions of the extensive parameters

$$\text{i.e. } U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

consider differential w respect to λ

$$\frac{\partial U}{\partial (\lambda S)} \Big|_{\substack{V \\ N}} \frac{\partial (\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial (\lambda V)} \Big|_{S,N} \frac{\partial (\lambda V)}{\partial \lambda} + \dots = U(S, V, N)$$

chain rule

this must be true $\forall \lambda$, incl $\lambda=1$

$$\frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \dots = U(S, V, N)$$

T $-P$ μ

so
$$U = TS - PV + \mu N$$

and
$$S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \left(\frac{\mu}{T}\right) N$$

note these are not differentials any more

let's see what the full derivative is

Last lecture: We ended our discussion with the Gibbs-Duhem relation which demonstrated the interdependence of intensive variables, i.e. you can express the change of one in terms of the other variable. In general, a simple system of r components has $r+1$ thermodynamic degrees of freedom

So our theoretical framework is thus:

We have a fundamental relation

$$U = U(S, V, N)$$

From this, we have partials

$$T = \left. \frac{\partial U}{\partial S} \right|_{V, N} = T(S, V, N) \leftarrow \text{equation of state}$$

$$-P = \left. \frac{\partial U}{\partial V} \right|_{S, N} = P(S, V, N) \leftarrow \text{equation of state}$$

$$\mu = \left. \frac{\partial U}{\partial N} \right|_{S, V} = \mu(S, V, N) \leftarrow \text{equation of state}$$

If we have all equations of state, we can recover the fundamental relation via the Euler relation

$$U = TS - PV + \mu N$$

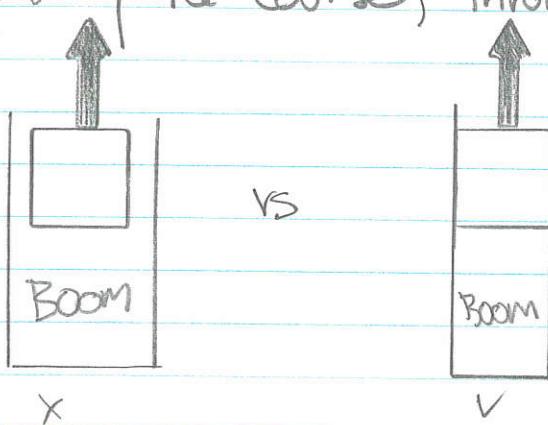
or by direct integration

$$dU = TdS - PdV + \mu dN$$

(you only need 2 out of three) (to within a const)

Where else is this important?

Engines (we'll be discussing these more at a later part of the course) involve hot, moving pistons



In order to function, we need a snug fit irrespective of temperature (Canada and California)

Obviously we could use the same material, but pistons are subject to other stresses which can make this impractical / expensive

Note that on the downstroke, P can be quite large, so what is

$$K_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T, N}$$

isothermal compressibility

i.e. how much does the volume change when pressure is applied and the temperature is fixed (i.e. held)?

Keep in mind that previously, we've observed that work and heat in processes vary depending on path.

8-5

Here we can understand why it might matter what is held constant

Let's think of two experiments



some material of interest



- apply heat w/ a torch
- box is completely rigid, volume fixed

vs



moveable piston, i.e. constant pressure



same material

- as before, apply heat
- this is now fixed pressure

After the experiments, what do we have?
We have less fuel, and hot material.



- there is also a change in volume
(constant pressure)

So work was done mgh

height
displacement

We have to spend more energy to get the temperature up in the second experiment

$$C_p \neq C_v, \gamma = C_p/C_v$$

8-7

So what is c in this case

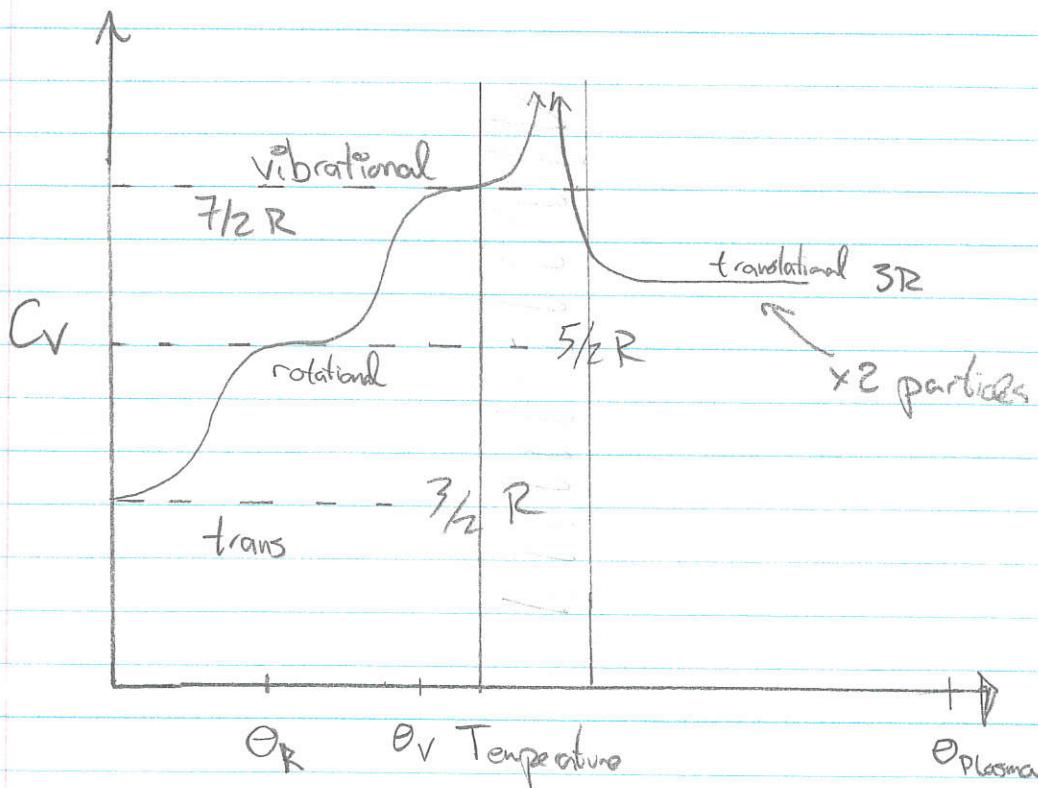
Recall for an ideal monoatomic gas we have

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

Each "degree of freedom" contributes

$\frac{1}{2}R$ to the "storage capacity" (equipartition theorem)

What about non-ideal, non-monatomic gas



Last lecture: We started to move away from the formal foundations of TD, and moved toward "observable", "common" derivatives such as

$$\alpha, \chi_s, \chi_T$$

There is a connection between these quantities and what we've discussed so far

α, χ_s, χ_T are 2nd derivatives of fundamental relations

We also discussed something more complicated than a non-ideal gas. As we relax restrictions on models, things get interesting.

van der Waals fluid

Let's begin by first writing the vdW - mechanical EOS

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Note the following

$$P(V-b) = RT - aV^{-2} \quad ()$$

$$P(V_N-b) = RT - a\left(\frac{V}{N}\right)^{-2}, \quad PV - Nb = NRT - aN\left(\frac{V}{N}\right)^{-2} \quad ()$$

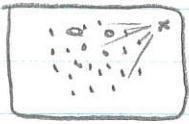
when $b=0 \quad \& \quad a=0$

$PV=NRT$

9-3

What about the a^2 ?

Recall there is both a repulsive and attractive region of a typical interaction potential. This reduces the pressure b/c it inhibits a molecule from hitting the wall as it is pulled toward the pack.



scales w number of pairs, $\frac{1}{\sqrt{r^2}}$
(thanks to Laplace)
Nobel Prize

So we have

$$\frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2} \frac{1}{T} \quad ①$$

and this is a problem!

$$\frac{1}{T} = ? \quad ② \quad (\text{need this for } S)$$

$$ds' = \frac{1}{T} du' + \frac{P}{T} dv'$$

Note that we enforce symmetric derivatives

$$\frac{\partial^2 s}{\partial v \partial u'} = \frac{\partial^2 s}{\partial u' \partial v'}$$

$$\left. \frac{\partial}{\partial v'} \left(\frac{\partial s}{\partial u'} \right) \right|_{u'} = \left. \frac{\partial}{\partial u'} \left(\frac{\partial s}{\partial v'} \right) \right|_{v'}$$

$\frac{1}{T}$ $\frac{P}{T}$

9-5

so taking the original form

$$\frac{P}{T} = \frac{R}{v'-b} - \frac{a}{v'^2} \left(\frac{1}{T} \right)$$

$\underbrace{\qquad\qquad\qquad}_{u'+a/v'}$

$$\frac{P}{T} = \frac{R}{v'-b} - \frac{a}{v'^2} \left(\frac{cR}{u'+a/v'} \right)$$

$$\boxed{\frac{P}{T} = \frac{R}{v'-b} - \frac{ack}{u'v'^2 + av'}} \quad (1)$$

EoS

$$\boxed{\frac{1}{T} = \frac{cR}{u'+a/v'}} \quad (2)$$

$$ds' = \frac{1}{T} du' + \frac{P}{T} dv'$$

Integrating

$$S = N R \ln \left[\left(\frac{V}{N} - b \right) \left(\frac{U}{N} + \frac{Na}{V} \right)^C \right] + NS_0$$

How do we get a and b ?

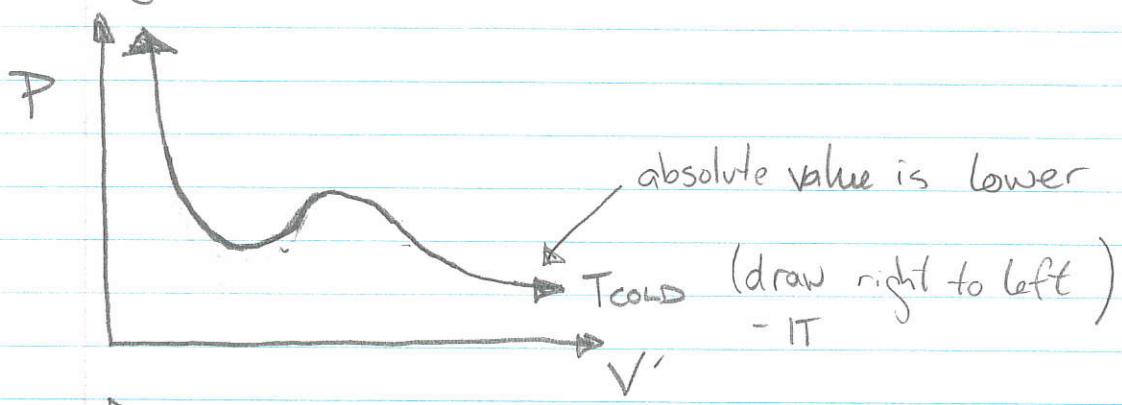
$$P = \frac{RT}{v'-b} - \frac{a}{v'^2} \quad (\text{original eqn})$$

At some point, you have collected data and fit it. You probably looked at something like Resistance, e.g. $V=IR$

Collect $P(T)$ at fixed v' for several v' , then fit.

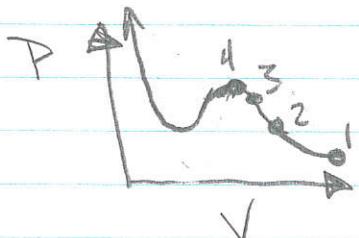
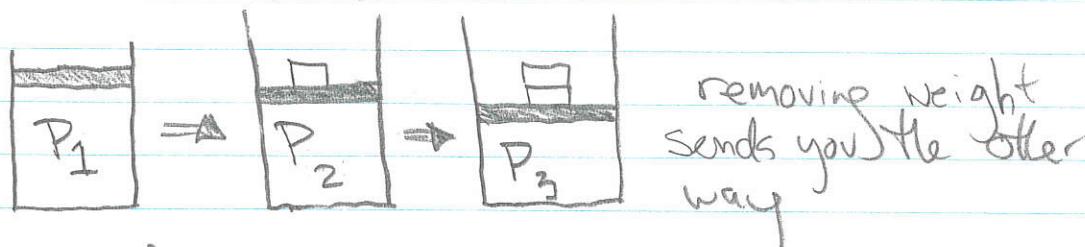
9-7

Again we have $P \& V$



note there is a minimum V' value due to hard sphere radius. There is now an inverted region (true for both axes)

Let's consider what it be like to compress such a fluid. At low density, large V' to compress the fluid I must apply a pressure. As I do this $P \uparrow$. To keep from going backward, that pressure must be maintained.



What about at point 4?

When I add more weight (pressure) the volume decreases but so does the pressure requirement! This causes the volume to go down again, along

Fix the S_0' foolishness

10-1

Last lecture: We started to look @ "not-so-simple" systems. We looked at the consequences of finite molecular volumes and intermolecular interactions. This is a more physically realistic model and we were rewarded w/ a phase transition.

Let's discuss some more

Mixture of an ideal gas

We have discussed mixing already in the context of the 2nd law of TD. We argued there is more configurational entropy in a mixed system than unmixed (there are more mixed configurations).

Recall

$$S' = S'_0 + R \ln \left[\left(\frac{U'}{U'_0} \right)^c \left(\frac{V'}{V'_0} \right) \right]$$

fundamental relation
for ideal gas in
entropy representation, molar
form

If I have two separate containers

U_L, V_L	U_R, V_R
S_{L,N_L}	S_{R,N_R}

$$\begin{aligned} U &= U_L + U_R \\ V &= V_L + V_R \\ N &= N_L + N_R \\ S &= S_L + S_R \end{aligned}$$

Once I remove the wall, particles can flow back and forth, energy is exchanged, temperatures equilibrate, pressure is uniform etc

If the system is isolated from the outside

10-3

We can write these sums as

$$S = \sum_j^k N_j S_{j_0} + \left(\sum_j^k N_j c_j \right) R \ln \frac{T_i}{T_0} + \sum_j^k N_j R \ln \left(\frac{V_j}{N_j V_0} \right)$$

$$U = \left(\sum_j^k N_j c_j \right) RT$$

This is our expression for the total entropy and total energy prior to the removal of the walls

What happens when the "walls fall down"? Suddenly, all V is accessible.

Each $V_j \Rightarrow V$



So

$$S = \sum_j^k N_j S_{j_0} + \left(\sum_j^k N_j c_j \right) R \ln \frac{T_f}{T_0} + \sum_j^k N_j R \ln \left(\frac{V}{N_j V_0} \right)$$

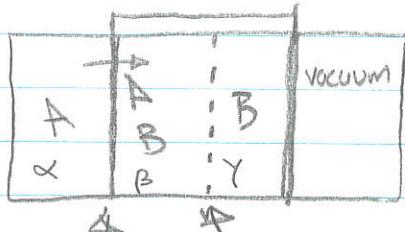
Although this might not seem like a big change (one variable), it is

$$V = V_1 + V_2 + \dots + V_k$$

$$\sum_j^k N_j R \ln \left(\frac{V_1 + V_2 + \dots + V_k}{N_j V_0} \right) = \sum_j^k N_j R \ln (V_1 + V_2 + \dots + V_k) - \sum_j^k N_j R \ln (N_j V_0)$$

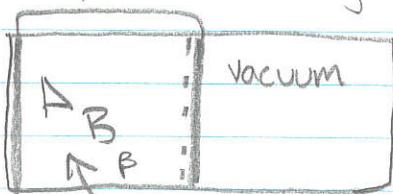
10-5

Move the handle to the left



$$\mu_{A,\alpha} = \mu_{A,\beta}, \quad \mu_{B,\alpha} = \mu_{B,\beta}$$

A passes through
 B passes through



Note $V_\alpha = V_\gamma$
since walls allow it, $P_\alpha = P_\gamma$

$A \& B$ are now mixed
they are in the same size volume as
before however.

Interestingly, the chemical potentials equivalence of the chemical potentials means

$$P_\beta = 2P_\alpha$$

Why is this?

At the final configuration it can be seen most clearly - two gases in the same volume, total pressure = Σ of the partial pressures So factor of $\times 2$

Consequence?

Pressures are then $P_\alpha + P_\beta + 0$ (vacuum)

$$P_\beta = 2P_\alpha + P_\gamma, \quad P_\alpha = P_\gamma \\ = 0 \Leftarrow \text{no net force, no work!}$$

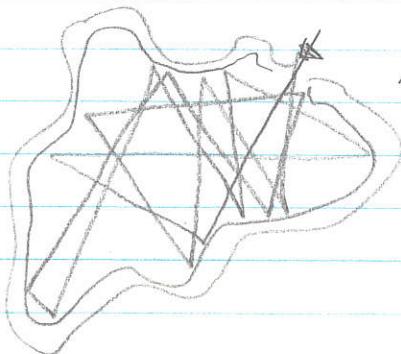
MIDTERM REMINDER

|| - |

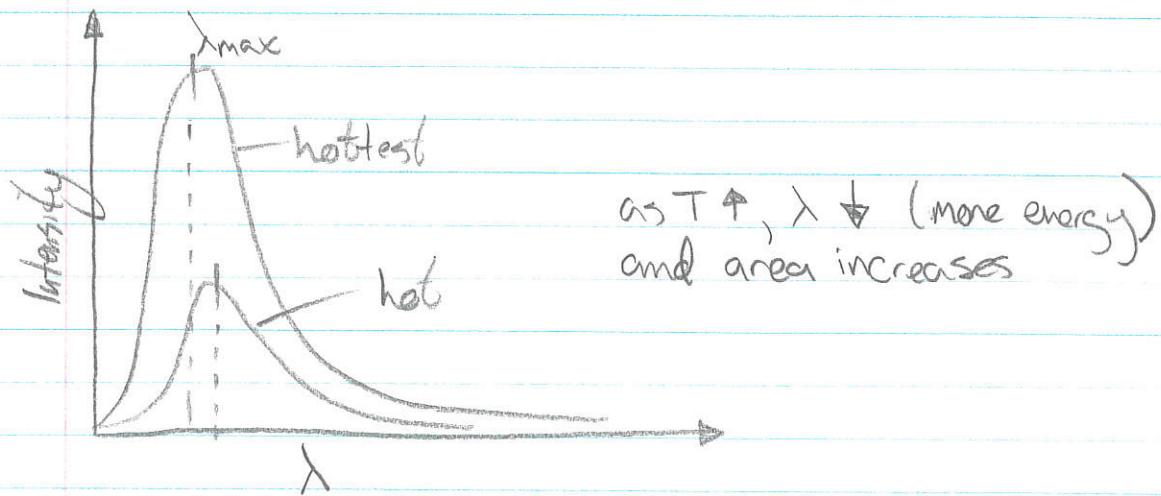
Last lecture: We quantified the entropy of mixing for an ideal gas. We showed it's importance for a cool experiment and a no so cool planet!

We ended discussing Black body radiation. Everyone is familiar with the phenomena, but can we say something about the thermodynamics?

Recall



photons are in thermal equilibrium w/ the cavity



Total power is $\int I(\lambda) d\lambda$

→ more area means brighter

Callen 3.6

11-2

Experimentally Stefan noted in 1879

$$U = bVT^4, P = \frac{U}{3V} \quad \begin{matrix} \text{radiation density,} \\ \text{comes from Maxwell's eqns} \end{matrix}$$

If you work out the radiation pressure from the sun hitting earth

Solar flux is about 1.4 kW/m^2 (solar cells!)

$$\text{then } P_{\text{sun}} \sim 10^{-5} \text{ Pa} = \underbrace{10^{-10} \text{ atm}}$$

10^6 less than a sound wave

→ thinking of pressure as an energy density is useful for thermodynamic potentials (coming up) and can be seen from unit analysis

$$\text{Euler } U = TS - PV + \mu N$$

$$[J] \quad [J/m^3][m^3]$$

And if you're not convinced there is energy in that volume, stick your head in a microwave!

Okay, back to our derivation

$$U = bVT^4, P = \frac{U}{3V}$$

Cullen Z.9

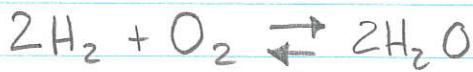
11-4

What about our chemist friends?

Up until this point we have worked w fixed mole numbers. Permeable and impermeable walls were able to restrict flows of particles, but the total numbers of say A & B did not change.

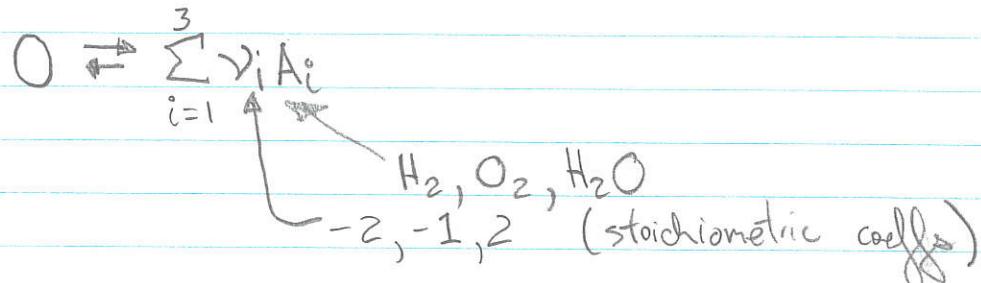
In Chemistry of course this does not happen

Consider the formation and dissociation of water



the arrows here are important
at equilibrium there is still dissociation and formation taking place, but the rates are equal

lets understand in terms of thermodynamics



Since chemical rxn change mole numbers

$$dS = -\sum_{i=1}^3 \frac{\mu_i}{T} dN_i \quad \leftarrow \text{components}$$

rewrite in terms of stoichiometric coefficients

$$dN_i = \nu_i d\hat{N}$$

Let's make the approximation that all of the species are quasi-ideal. Quasi in the sense that their EOS are given by $c = 5/z$, but though addition or removal of energy I can inter-convert

In practice this isn't normally done, but it's instructive because it lets me connect p_i in terms of $P \& T$ straightforwardly

$$\mu_i = RT [\ln p_i + \ln x_i + \phi_i(T)]$$

↑ ↓ ↗
 pressure of the container N_i/N arbitrary function
 (for const T, P)
 doesn't matter

$$\sum_i \gamma_i \mu_i = 0 \quad (\text{at equilibrium})$$

so we have

$$\sum_i \gamma_i \ln x_i = - \sum_i \gamma_i \ln P - \sum_i \gamma_i \phi_i(T) - E_{\text{diss}}/RT$$

$$\sum_i \ln x_i^{\gamma_i} = - \sum_i \ln P^{\gamma_i} - \sum_i \gamma_i \phi_i(T) - E_{\text{diss}}/RT$$

$$e^{(\ln x_1^{\gamma_1} + \ln x_2^{\gamma_2} + \dots)} = e^{(\ln \bar{P}^{\gamma_1} + \ln \bar{P}^{\gamma_2} - \sum_i \gamma_i \phi_i(T) - E_{\text{diss}}/RT)}$$

$$e^{\ln x_1^{\gamma_1}} e^{\ln x_2^{\gamma_2}} = e^{\ln \bar{P}^{\gamma_1}} e^{\ln \bar{P}^{\gamma_2}} K(T)$$

$$\prod_i x_i^{\gamma_i} = P^{\sum_i \gamma_i} \underbrace{K(T)}_{\text{Law of mass action}}$$

$\nwarrow \pi$ product

$$K(T) = \exp \left[- \sum_i \gamma_i \phi_i(T) - E_{\text{diss}}/RT \right]$$

Equilibrium rate constant (Arrhenius etc)

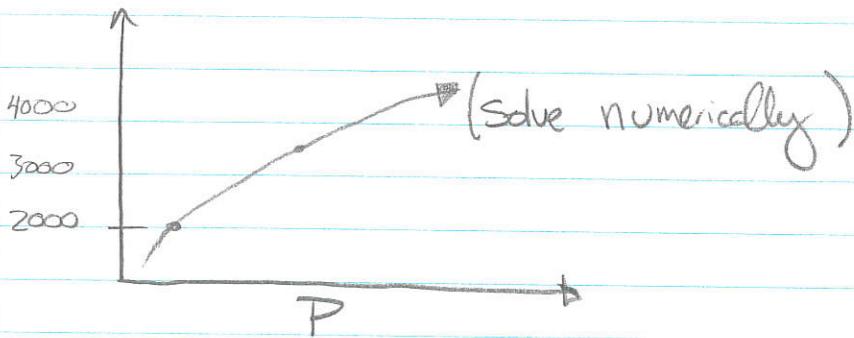
What is E_{diss} in terms of temperature?

$$K_B T = E_{\text{diss}} \leftarrow 52,200 \text{ K}$$

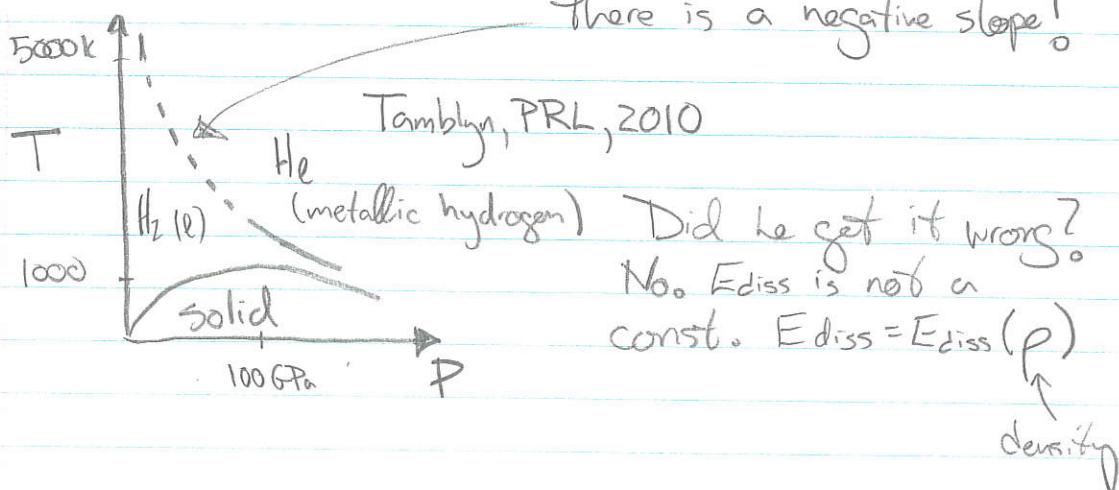
Note that there is full dissociation well before this, so don't think in terms of a mechanical escape velocity! This is a common mistake made by physicists in particular (and mathematicians, and engineers...)

(on Thursday we'll take a bit of time to look at velocity distributions)

- ② It looks like as you increase the pressure, the dissociation increases ($0.0001 \rightarrow 1 \text{ atm}$ the temperature required to reach 0.5 goes up from $\sim 2000 \text{ K} \rightarrow 3500 \text{ K}$)



BVT



SURVEY, MIDTERM TIME CSD

12-1

Midterm review: What have we done so far in this course?

- ① We learned about the need for a macroscopic theory of equilibrium properties.

Even though I know atoms exist, for any reasonable system there are far too many to think about all degrees of freedom. Instead we focus on macroscopic observables. This is equivalent to an average in time and space

- ② We discussed the concept of equilibrium in the thermodynamic sense. A system at equilibrium does not depend on history and does not change in time.

- ③ We discussed examples of macroscopic observables. Length, volume, mole number, temperature, etc

Fluctuations (which are always present when $N \gg 1$) due to elementary excitations in the system should be small compared to these quantities

$$\frac{\delta L}{L} \ll 1$$

We also identified two classes of variables

extensive: $S, U, V, N \leftarrow$ additive over sub-sections
intensive: $T, P, \mu \leftarrow$ not additive

12-3

other times it was a line and you had to connect it to your inner grade 8 self to find $P(V)$. And finally, in some cases you were told it was an adiabatic process. If the system was made of cottage cheese, experiments would be needed. For an ideal gas:

$$\boxed{PV^{5/3} = \text{const}, \quad (\text{monatomic})}$$

so we know

$$PV^{5/3} = P_i V_i^{5/3} = P_f V_f^{5/3}$$

we derived this
by realizing $dQ = TdS$,
 $\therefore dQ = 0$ implies $dS = 0$
 $S = \text{const}$ for FR

$$P = P_i V_i^{5/3} V^{-5/3}$$

this is $P(V)$

We can then use this to integrate to find work

What about dQ ? For a particular case of the motor in the ideal gas, we were told through observation

$$dU = \frac{3}{2} V dP \quad (\text{const volume})$$

Here no work was done b/c volume is constant, so it can only be heat

$$dQ = \frac{3}{2} V dP$$

The partials are functions of the extensive parameters

$$T = T(S, V, N), P = P(S, V, N), \mu = \mu(S, V, N)$$

EOS

$$\frac{T}{T} = \frac{1}{T}(U, V, N), \frac{P}{T} = \frac{P}{T}(U, V, N), -\frac{\mu}{T} = -\frac{\mu}{T}(U, V, N)$$

Having the set of EOS is equivalent to having the FR. Why?

$$U = TS - PV + \mu N$$

$$S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \frac{\mu}{T}N$$

both are Euler eqn

If you have EOS, which are $f(S, V, N)$ or $g(U, V, N)$, by substitution we recover

$$U = U(S, V, N) \text{ or } S = S(U, V, N)$$

- ⑦ We also noted the Gibbs-Duhem relation, which showed the interdependence of some intensive parameters

A change in chemical potential can be thought of as

$$d\mu = -SdT + VdP \quad \left(S' = \frac{S}{N}, V' = \frac{V}{N} \right)$$

12-7

$$C_V = \left. \frac{T}{N} \frac{\partial S}{\partial T} \right|_{V,N} \quad \begin{array}{l} \text{specific heat at constant} \\ \text{volume} \end{array}$$

$$C_P = \left. \frac{T}{N} \frac{\partial S}{\partial T} \right|_{P,N} \quad \begin{array}{l} \text{specific heat at constant} \\ \text{pressure} \end{array}$$

We showed that it matters significantly what is held const in different experiments

e.g. if volume can change, work is likely to be done (unless there is a vacuum...)

If heat is allowed to flow in or out of a system the energy balance is not the same

And finally, we noted these observable derivatives are really just 2nd derivatives of the FRS.

For our old friend, the ideal gas

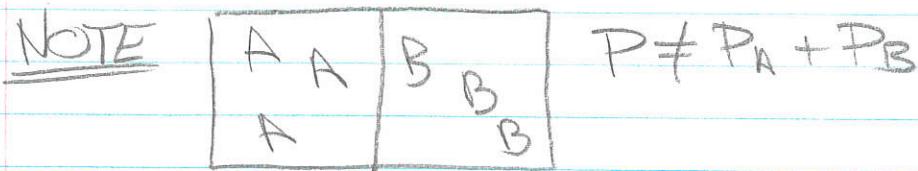
$$\alpha = \frac{1}{T}, \quad K_T = \frac{1}{P}, \quad C_V = cR, \quad C_P = (c+1)R$$

$$\boxed{\frac{K_T}{K_S} = \frac{C_P}{C_V}, \quad C_P - C_V = VT \frac{\alpha^2}{K_T}} \quad \begin{array}{l} \text{always} \\ \text{true} \end{array}$$

(I think we didn't get to this part of my notes that day, but don't worry...)

12-9

(10) We discussed mixtures and noted that in the limit of low densities and weak interactions, the partial pressure approximation was a good one



Furthermore, we saw that when going from an unmixed system to a mixed one, there was an increase in the total entropy of the system. This is called the entropy of mixing and is consistent with the notion that entropy is maximized in the absence of internal constraints

$$\left[-R \sum_j N_j \ln \frac{N_j}{N} \right]$$

Entropy of mixing argument of \ln is < 1
 $\therefore (-)(-) = +ve$ always. 2nd Law ✓

We showed a clever way to achieve reversible mixing ~~at~~ constant entropy

This is different than an irreversible process where entropy increases.

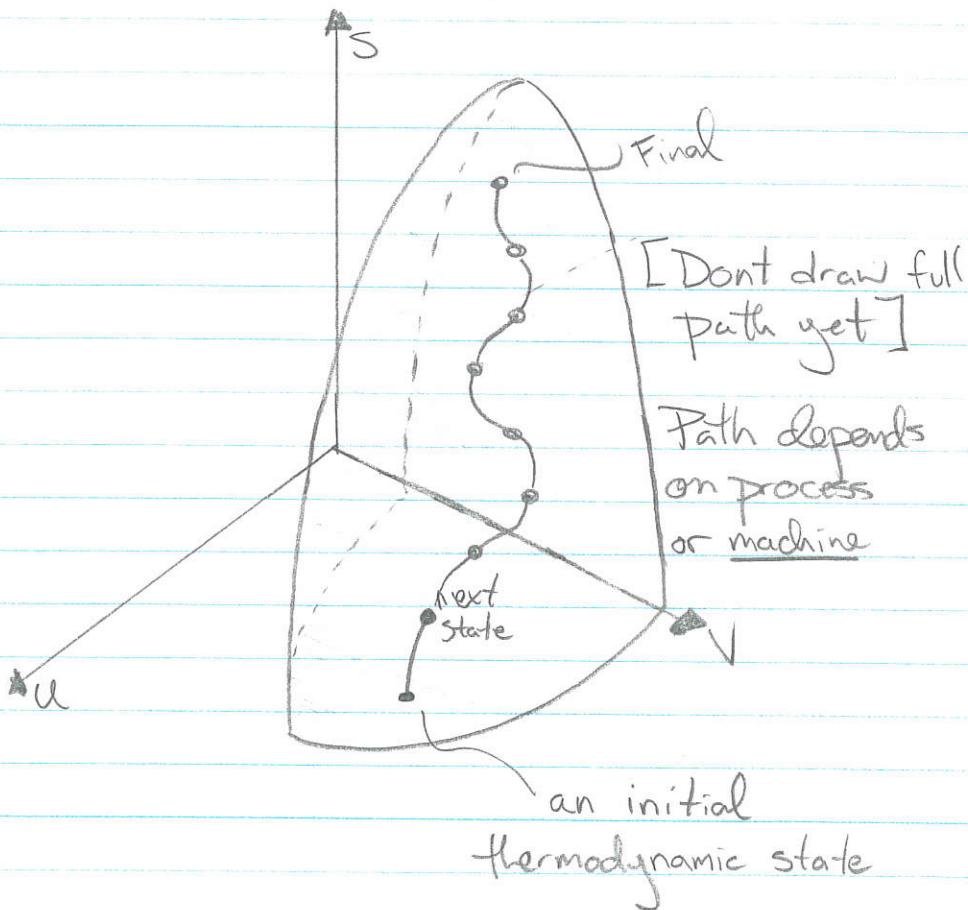
Finally, we explored some interesting systems incl black body radiator, chemical processes and LOMA

Up to this point, we have focused on equilibrium properties

We hinted at the possibility of considering deviations from equilibrium in the notion of a quasi-static process

You will recall quasi-static means slow compared to the relaxation time of the system

Such processes "connect" equilibrium states

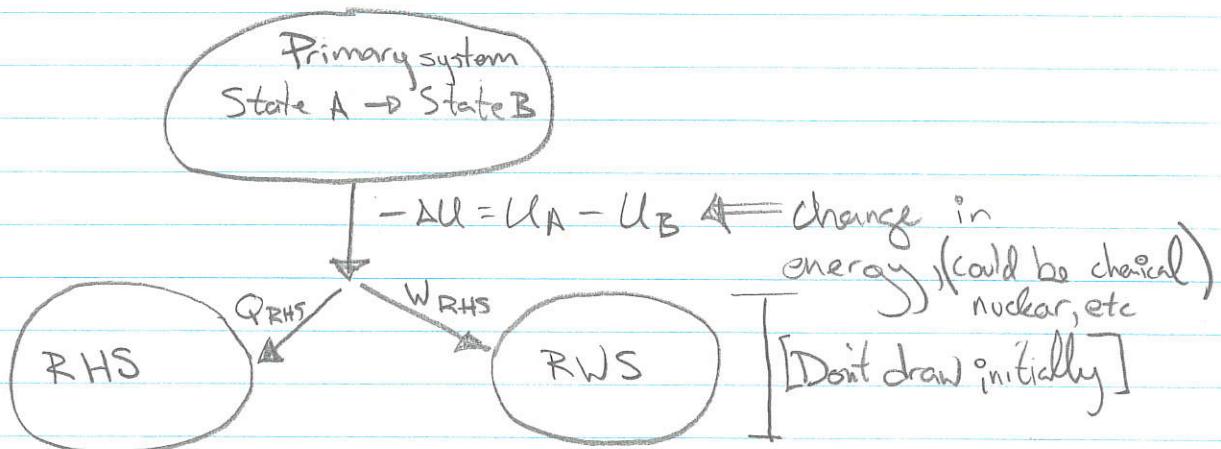


The "state" represents the average for a given set of constraints. This is different than a single particle state. When constraints are allowed to relax, it moves to the new equilibrium. [Draw next state]

13-3

A question you might ask if you are required to design a machine (or pay the fuel/electricity cost) is how much work can I extract?

Maximum Work Theorem



When the system goes from A → B, its internal energy changes. We would like to use this energy ($-ΔU = U_A - U_B$). Recall

$$dU = dQ + dW$$

So, whatever leaves the primary must do so as heat or work.

Let's attach two devices. One which can add or remove heat, and another which can add [Draw] or remove work. In practice, a reversible work source does not exist.

e.g. - Mechanical spring (compression)
 - magnetic levitation
 - pulley and weight

] all have
 } less pathways
 } ∴ heat

Back to the task at hand.

We would like to live in a world where all of the ~~All~~ goes into work (heat is not useful), but we know inevitably some will be lost. (we've divided out that portion into our RHS)

$$dU_p + dQ_{RHS} + dW_{RWS} = 0$$

energy leaving heat loss
 in process in process
 $dS_{\text{total}} \geq 0$ (2nd Law)

$$dS_{\text{total}} = dS_p + dS_{RHS} + dS_{RWS}$$

$$dS_p + dS_{RHS} \geq 0$$

0, by defn

RHS = rigid, impermeable, fast relaxations, $\therefore dQ = TdS$

$$dS_p + \frac{dQ_{RHS}}{T_{RHS}} \geq 0$$

$$TdS_p + dQ_{RHS} \geq 0$$

$$TdS_p - dU_p - dW_{RWS} \geq 0$$

$$dW_{RWS} \leq T_{RHS} dS_p - dU_p$$

The maximum work I can extract depends (is limited by) the change in entropy of the primary and temperature of the heat source/sink.

* See Keynote!

14-0

Last lecture We began discussing using physical processes / changes to do useful work. We showed that any time there is a change of internal energy (ΔU) in our primary source (chemical, mechanical, or nuclear change) some of the released energy can be used for work, while some is forever lost as heat.

All such processes have a characteristic maximum thermodynamic efficiency. Better gears and lighter parts cannot get around this (though better ideas may...)

Let's look at some specific examples:

[Note for future]

$$dW_{RHS} = \frac{T_{RHS}}{T} dQ - dU$$

(max)

$$\text{mention } dQ = T dS$$

$$\text{so } \frac{dQ}{T} = dS$$

$$\Delta S = S_f - S_i$$

The fraction of extracted heat that can be converted into work is

$$\varepsilon = \frac{dW_{RHS}}{-dQ} = 1 - \frac{T_{RHS}}{T}$$

Note, if $T_{RHS} = T$

$\varepsilon = 0 \leftarrow$ perpetual motion machine of the 1st kind!

To optimize efficiency, T_{RHS} must be as low as possible. We need a very efficient heat sink. Is that enough?

Let's think of the 1st thermodynamic engine, the steam engine. We know it involves boiling water, so $T = 373\text{ K}$.

$$\text{What is } \varepsilon = 1 - \frac{300}{373} = 0.2$$

20% seems low. What are we missing?
(In practice 1-10%)

For one thing it is silly to restrict ourselves to ambient pressure. What is the purpose of a kitchen pressure cooker? T_{boil} increases.

If we raise the boiling point by 300° , $\varepsilon = 0.55$, i.e. 55% efficient.

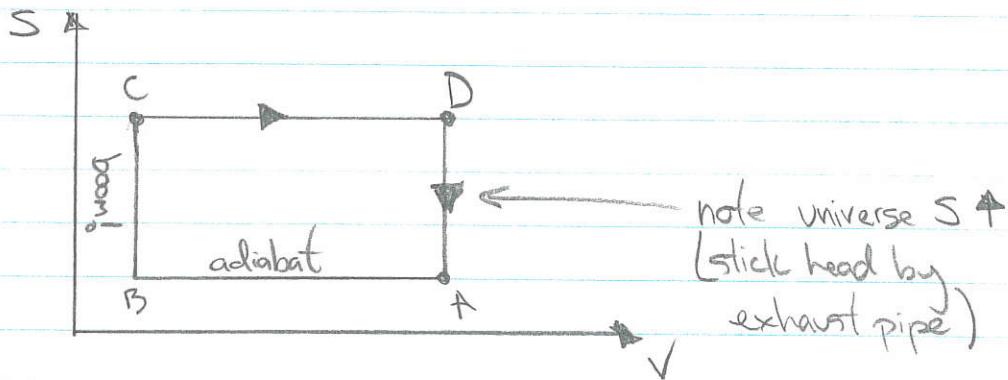
It is also possible to make use of heat/pressure at other

14-2

$C \rightarrow D$ Power stroke, piston is allowed to move again. Due to high pressure it pushes back. You can place a load on it during this stage (connect a rope) and it will pull

$D \rightarrow A$ exhaust and reset

Let's now think of the same cycle another way
Assume $U = cNRT$, $c > 3/2$ (not monoatomic)



$A \rightarrow B \quad Q_{A \rightarrow B} = 0 \quad (\text{adiabat})$

$$W_{A \rightarrow B} = c(P_B V_B - P_A V_A)$$

$$P_B V_B^\gamma = P_A V_A^\gamma$$

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

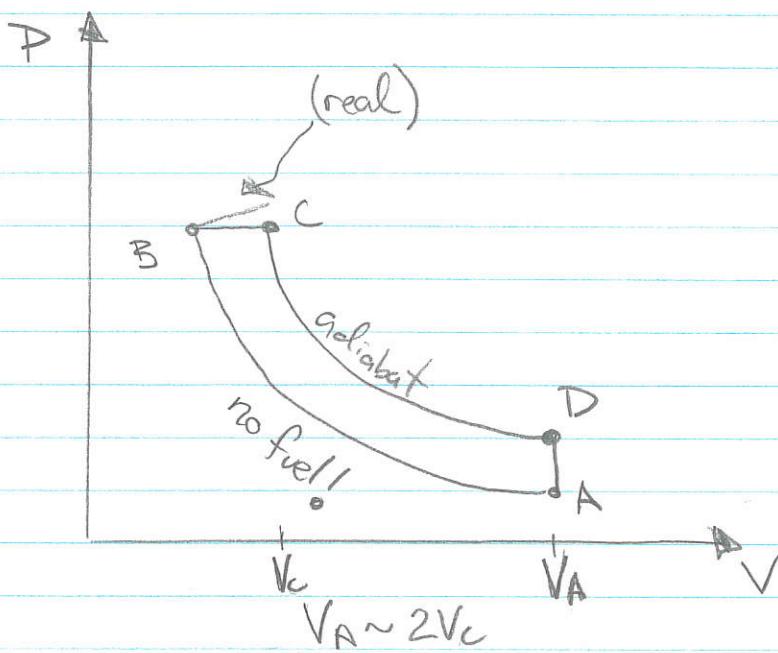
$B \rightarrow C \quad dW = 0 \quad (dV = 0)$

$$Q_{B \rightarrow C} = U_C - U_B$$

$$= c(P_C - P_B)V_B$$

Pre-ignition, good or bad?

In the Otto cycle, preignition limits efficiency. Rudolf Diesel recognized this and used a better idea to get around this limit.



$A \rightarrow B$ piston compresses air adiabatically
(no fuel present)

B - fuel injected

$B \rightarrow C$ heat from air causes vaporization and burning of fuel
(unlike the very volatile fuel used in Otto engines, diesel fuel does not easily convert to a gas)

$C \rightarrow D$ with fuel spent, allow for adiabatic expansion

$D \rightarrow A$ exhaust and reset

Let's put in some numbers:

$$r = 9 \text{ (Otto)}, r_c = 2 \quad \left(\begin{array}{l} \text{no } r_c \text{ for Otto} \\ \text{b/c burns at const V} \end{array} \right)$$

$$\epsilon_{\text{Diesel}} = 0.51 \quad \text{worse than Otto!}$$

→ r_{Diesel} is bigger than Otto though

$$r = 20 \text{ (Diesel)}, r_c = 2$$

$$\boxed{\epsilon_{\text{Diesel}} = 0.65}$$

Differences between Otto & Diesel

Otto - combustion at constant volume

Diesel - " " " pressure (almost)

Otto, variations of fuel-air mixture vs
 Diesel variations of fuel at constant mass of air. More pedal has different effect.

Diesel engines operate at higher temperatures than gas engines; they are built to withstand greater stresses (more durable), so they tend to last longer. More expensive materials though.

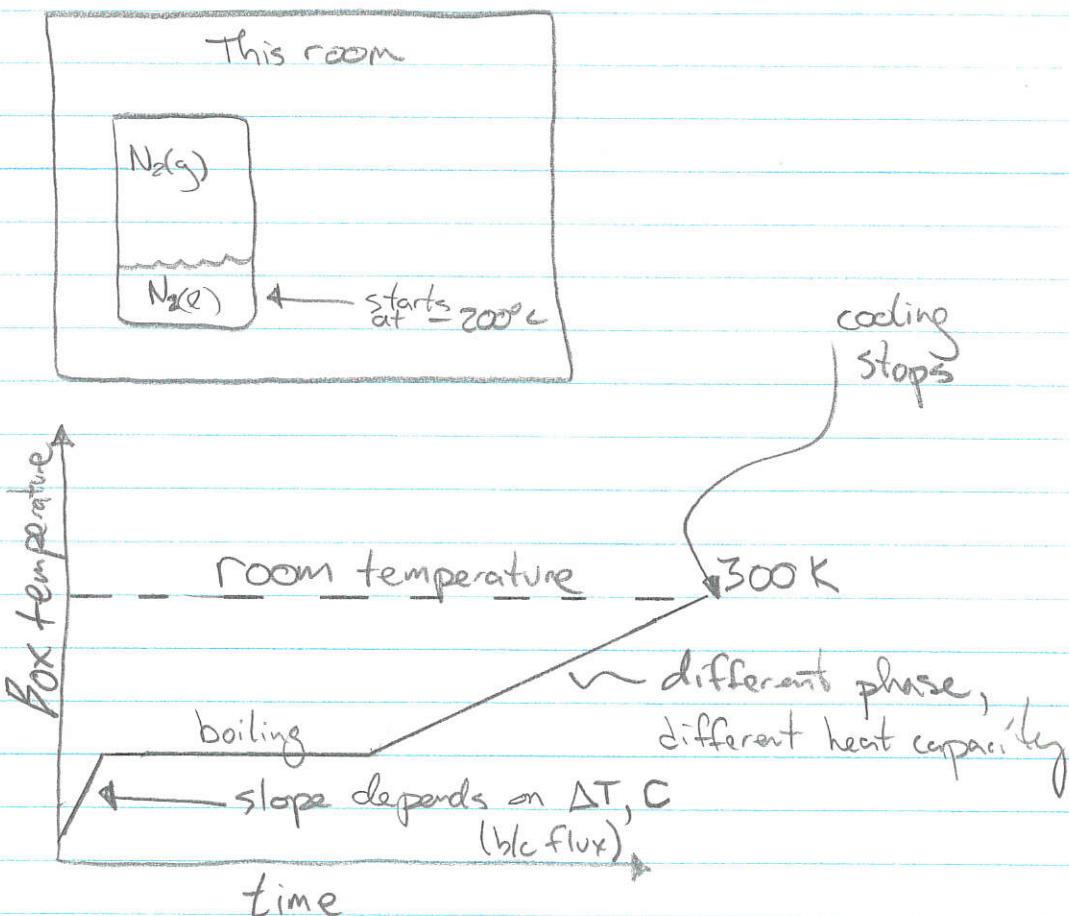
The fact that it is the heat provided in the compression stroke which is responsible for vaporization means fuels w/ lower volatility can be used. Why does volatility matter?

Last lecture: I convinced you that engines can convert heat into work. We saw that different designs have different, limiting thermodynamic efficiencies.

Other common examples of heat \leftrightarrow work converters are refrigerators. In these machines though, work is done to move heat.

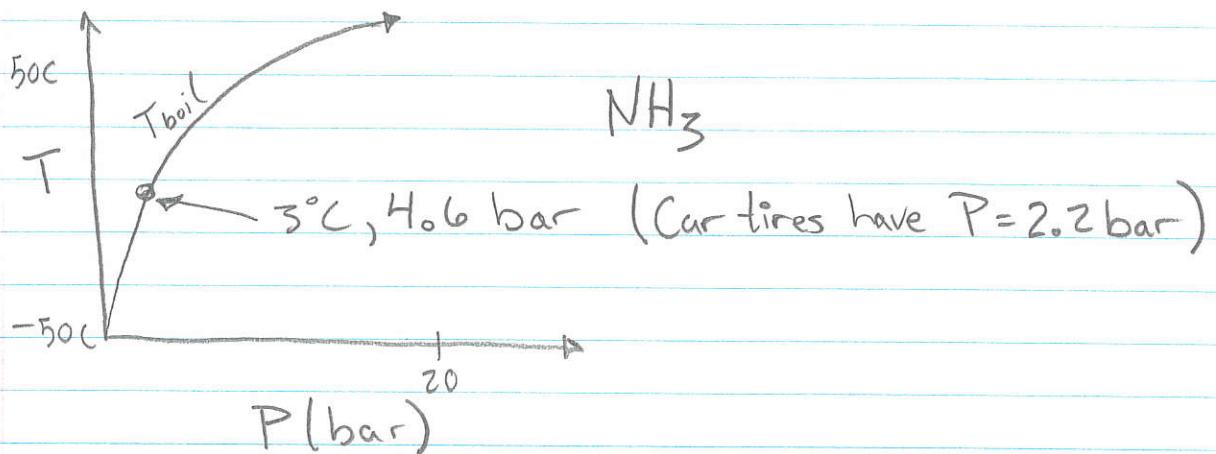
Let's understand this:

(Liquid nitrogen boils at 77K)

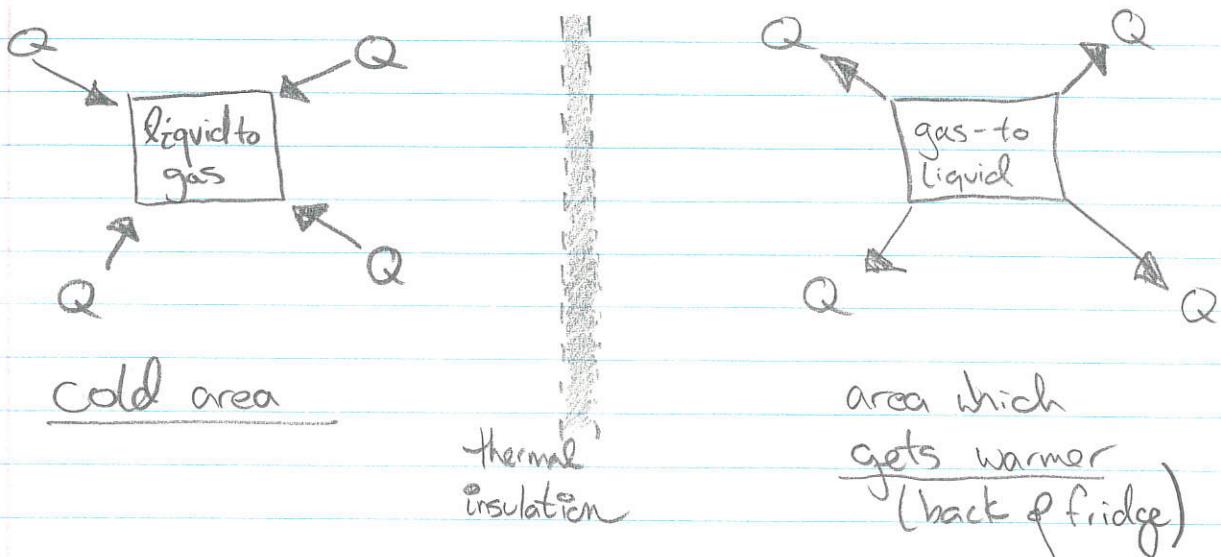


15-3

What if I use a material w/ a more reasonable P_{boil} behaviour [N₂ isn't unreasonable]



If I use NH₃ as a refrigerant, with modest application of pressure, I can force a gas-liquid transition. Cycling over and over again lets me remove heat.



$$\dot{\epsilon}_r = \frac{(-dQ_c)}{(-dW_{RWS})} = \frac{T_c}{T_h - T_c}$$

Note, when $T_h = T_c$, $\dot{\epsilon}_r \uparrow \infty$.

Why? No work needs to be done.
Also, $T_c \neq 0$, $\dot{\epsilon}_r \neq 0$. It's hard to cool off.

15-5

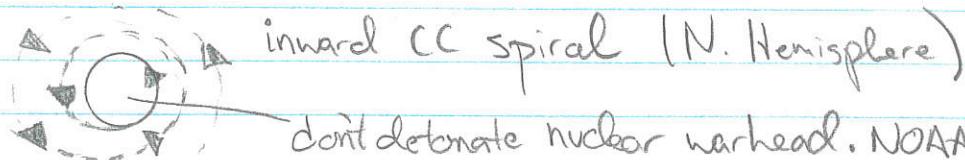
With a heat pump, $\epsilon_p = 146 \leftarrow$ very efficient

Cold day? $T_c = -20^\circ\text{C}$, $\epsilon_p = 7$

Huge drop. Once you factor in "engineering losses" (recall vehicle efficiency) and installation costs, most people find this impractical for home use. Industrially they are not uncommon though.

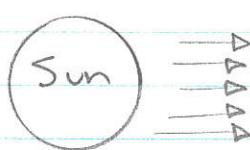
Let's think bigger -- Another heat engine

- Cyclones, a.k.a. Hurricanes, Typhoon
- rotate about low pressure region

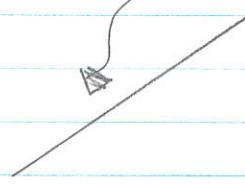


- Seen on Mars & Neptune

- Tropics get more sunlight, more heat



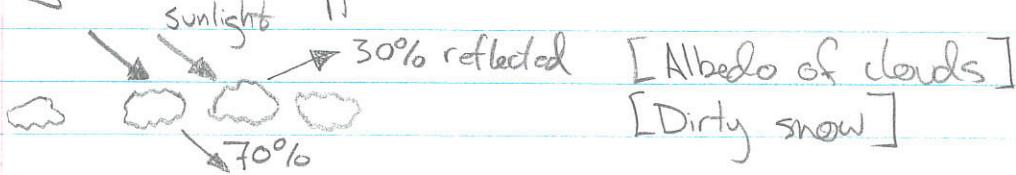
vs



Some light, more area

When there is a temperature imbalance, we know work is possible.

How do we get heat from the sun? The greenhouse effect.

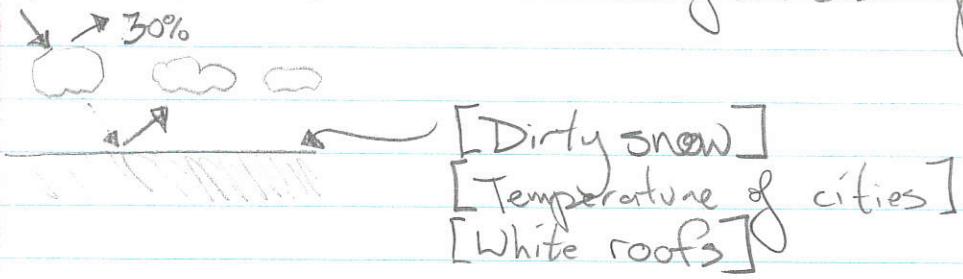


Last lecture: We discussed machines which can convert work (e.g. electrical) to move heat from one location to another. Useful for refrigeration and industrial scale heating (heat pumps)

We discussed a very large heat engine called the atmosphere. Why is this system interesting?

- ① I live there
- ② unequal heating (tropics vs N. Pole), day/night
- ③ It's changing due to our activities

We ended w/ an intro to greenhouse effect.



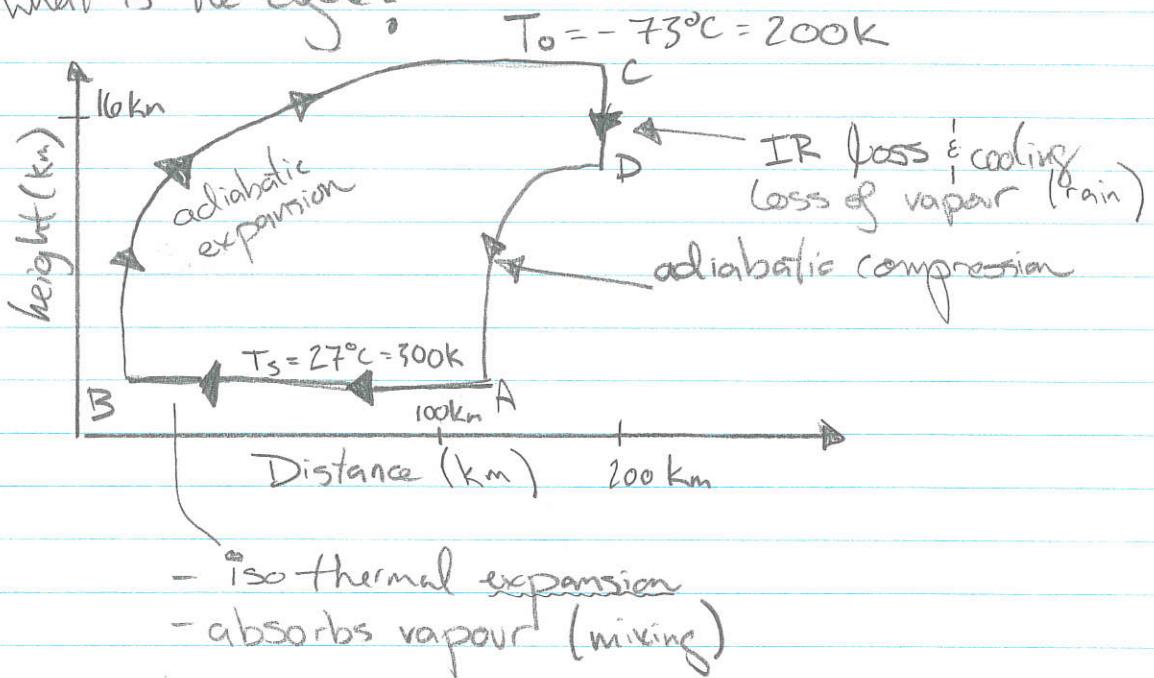
➡ Earth receives constant supply of energy which generates entropy.

A significant amount goes into mixing dry air w moist air. In fact, if not for this "sink", there would be so much atmospheric turbulence that air travel would not be possible.

So water is both a culprit and a saviour in terms of entropy.

* (insert cyclone intro) [p. 15-5]

What is the cycle?



At equilibrium, cyclone heat generation must equal dissipation

Incoming energy goes as wind speed $\sqrt{}$
(heat transfer from surface)

Dissipation happens through wind-surface friction.

To a first approximation, it can be shown

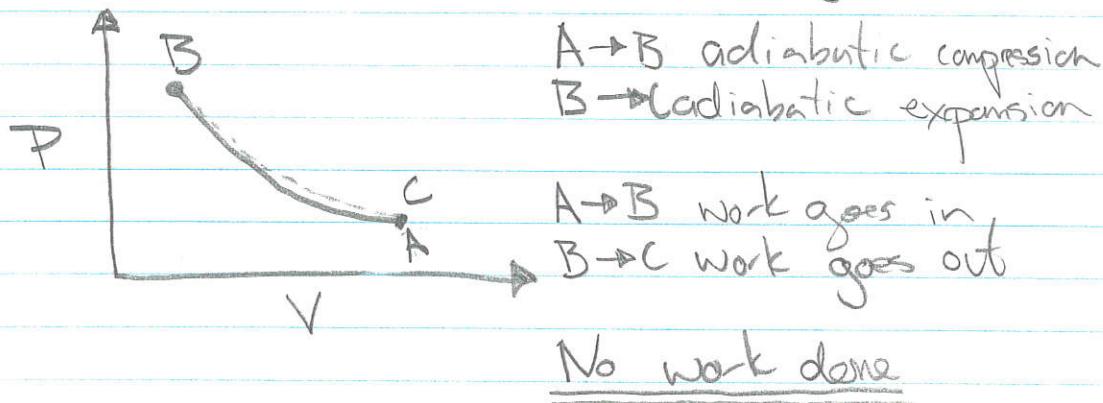
16-4

along this leg, the Carnot engine does work on the surroundings. This is part of the "power stroke" we saw in the Otto and Diesel cycles.

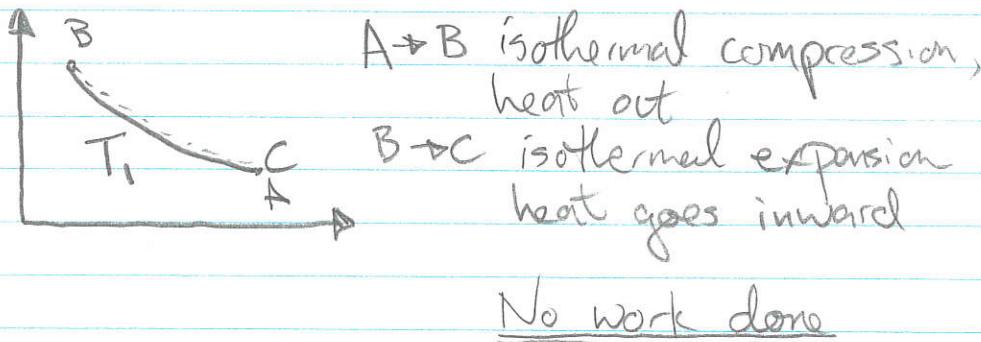
- D \rightarrow A hot reservoir detached, adiabatic expansion continues

Note the importance of the reservoirs

An "alternate, terrible" Carnot cycle



What about isothermal?



If's only in the full cycle, where we allow for heat transfer from hot \rightarrow cold where work can be done. In a cyclone, that heat is moving from surface to upper atmosphere (low T) [The Day after tomorrow]

17-2

$$P = P_d + e$$

$$\text{So, } \rho = \frac{P - e}{R_d T} + \frac{e}{R_v T}$$

$$\rho = \frac{P}{R_d T} \left[1 - \frac{e}{P} (1 - \varepsilon) \right]$$

$$\text{where } \varepsilon = \frac{R_d}{R_v} = \frac{M_w}{M_d} = 0.622$$

Then

$$P = \rho R_d T_v$$

$$T_v = \frac{T}{1 - \frac{e}{P} (1 - \varepsilon)}$$

T_v is called the "virtual temperature"

It is the temperature dry air would need to be to have the same density as a parcel of moist air. $T_v > T$. The higher T_v (on a map), the more moist the air is.

The issue of different densities of "air parcels" has an important consequence: bouyancy. Cold, dense, dry air vs warm, moist air

cold front >>>

<< warm front

Warm is lifted. Saturation is temperature dependent. Adiabatic expansion: rain. [Non-bouyancy]

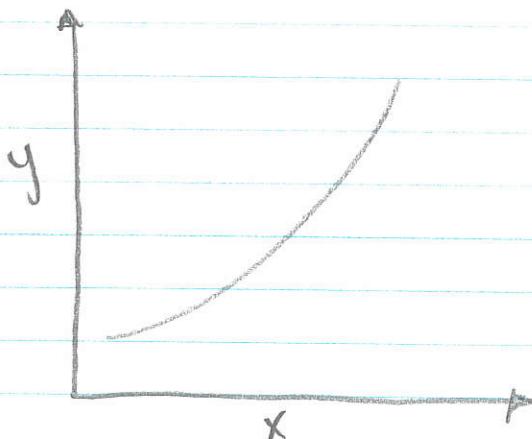
Up to this point, we have stressed the idea of maximizing entropy and conserving energy in isolated systems. Two options: max S at fixed U, or min U at fixed S.

What about cases where energy is not conserved?

What about cases where the system is connected to the rest of the Universe? Do we need to treat the whole of creation as our "system"?

To proceed, we make use of the Lagrange Transformations.

Consider $Y = Y(x)$



This function has a dependent variable: Y and an indep variable: X

We can invert it, $X = X(Y)$

This function also has a slope

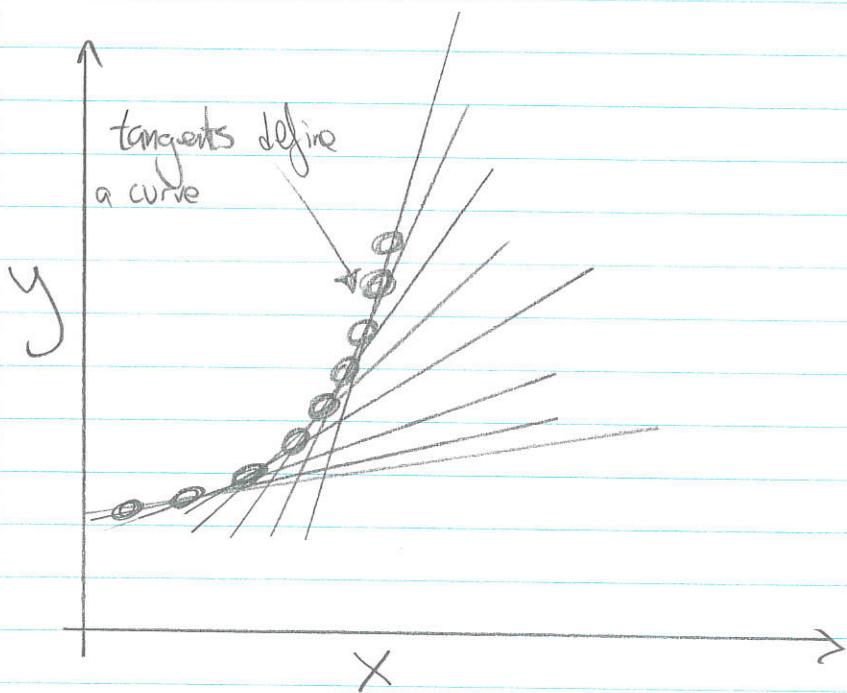
$$P \equiv \frac{\partial Y}{\partial X}$$

Compare what I have written to

$$U = U(S, V, N) \text{ or } S = S(U, V, N)$$

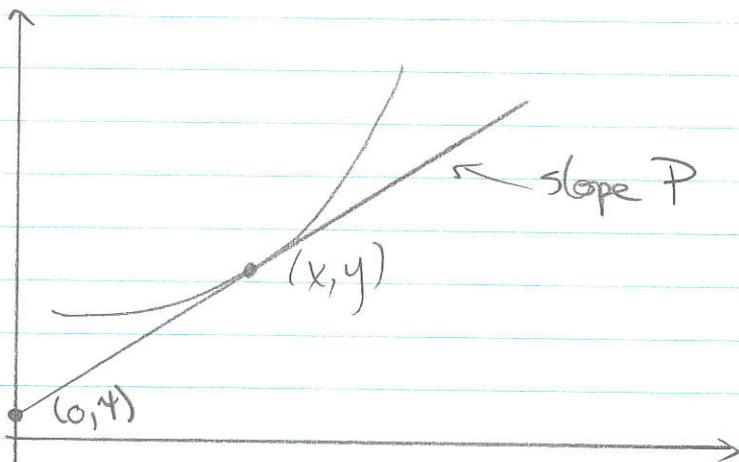
invertible

18-3



You are used to thinking of ordered pairs (x, y) which satisfy a particular $y(x)$

What if we think in terms of tangents?



If I record all $y \in P$ which are tangential to my curve, I will have all of the same information.

$$\text{Note : } \psi = Y - P X$$

$$d\psi = dY - dPX - PdX$$

↑ since $P \equiv \frac{dY}{dX}$

~~$$d\psi = PdX - dPX - PdX$$~~

$$d\psi = -dPX$$

$$-X = \frac{d\psi}{dP} \quad \leftarrow \text{this will be important going forward}$$

This is a relation of an original extensive parameter in terms of the new "potential" and an intensive parameter.

To go back and forth:

$$Y = Y(x) \quad \leftarrow \text{e.g. S or U}$$

evaluate intensive parameter

$$P = \frac{dY}{dX}$$

$$\text{Use } \psi = -PX + Y$$

Elimination yields

$$\psi = \psi(P)$$

Before we go further let's discuss why such a mixed transformation is desirable

Let's suppose I do an experiment where U is not constant, and S is not constant. Such a system is an "open" system.

What is held fixed (something must be...)

Different options

T, P, μ, B etc
 $\uparrow \quad \uparrow \quad \uparrow$
 $S \quad V \quad N, I$

only one of each pair

so $\gamma(T, P, \mu, B)$ is ok

but $\gamma(T, S, P, V, \mu, N, B, I)$ not ok

$\gamma(T, V, N) = \text{ok.}$

↑
 T rather than S
 no P
 no μ ✓

How would we make such a transform?

Start w/ $U = U(S, V, N)$

$$T = \frac{\partial U}{\partial S} \Big|_{V, N}$$

$$\gamma = U - TS, \text{ gives } \gamma = \gamma(T, V, N)$$

Last lecture: We began our discussion of thermodynamic potentials.

Thermodynamic potentials are used to study the equilibrium properties of systems where the energy is not fixed and are not isolated.
So far we have looked at

$$F = F(T, V, N) \leftarrow \text{Helmholtz}, F = U - TS$$

Let's see what we can do with this

Recall

$$U = U(S, V, N)$$

$$dU = TdS - PdV + \mu dN$$

$$\text{note } d(TS) = TdS + SdT$$

$$TdS = d(TS) - SdT$$

$$\text{so } dU = d(TS) - SdT - PdV + \mu dN$$

$$dU - d(TS) = - SdT - PdV + \mu dN$$

$$d(U - TS) = - SdT - PdV + \mu dN$$

$$\Rightarrow \boxed{dF = - SdT - PdV + \mu dN} \quad \text{differential form of } F$$

Know how to derive

Again, we wish to study a system w fixed variables

Equilibrium properties when S, P, N are held fixed

Start with $U = U(S, V, N)$

$$\begin{array}{c} \uparrow \\ P \end{array}$$

$$\frac{\partial U}{\partial V} \Big|_{S, N} = -P$$

Enthalpy (Helmholtz?)

So $H = U - (-PV)$

$$\boxed{H = U + PV}$$

where $H = H(S, P, N)$

In practice, what comes next? i.e. I have $U(S, V, N)$ so simply inserting

gives $H = H(S, V, P, N) !?$ incorrect

look @ EOS

$$= -P = P(S, V, N)$$

$$\text{invert, } V = V(S, P, N)$$

$$\text{so } H = U(S, V, N) + P V(S, P, N)$$

↑
insert $V(S, P, N)$ here

what about the differential form?

the "porous plug" is a material which lets material through but allows for $\Delta P \sim$ odd wall

To change $V_L' \rightarrow 0$ (i.e. push all the gas through)

$$W = - \int_{V_{L_i}}^0 P_L dv' = P_L V_{L_i}$$

constant

(again, depends on the plug)

Here things get a little iffy, b/c we are departing from equilibrium phenomena. Maintaining a specific P_L depends on compression rate and diffusion rate.

On expansion side, the opposite is true

$$W = - \int_0^{V_{R_f}} P_R dv' = P_R V_{R_f}$$

Assuming adiabatic walls (\bar{w} surroundings)
change in internal energy is due to work

$$U_f' - U_i' = P_L V_L' - P_R V_R'$$

which gives

$$U_i' + P_L V_L' = U_f' + P_R V_R'$$

 initially, all gas is on the left
so $U_i' = U_L'$

at the end, all gas is on the right
so $U_f' = U_R'$

19-7

$$dT = \frac{1}{C_p} (T\alpha - 1) dP$$

Let's analyze two cases:

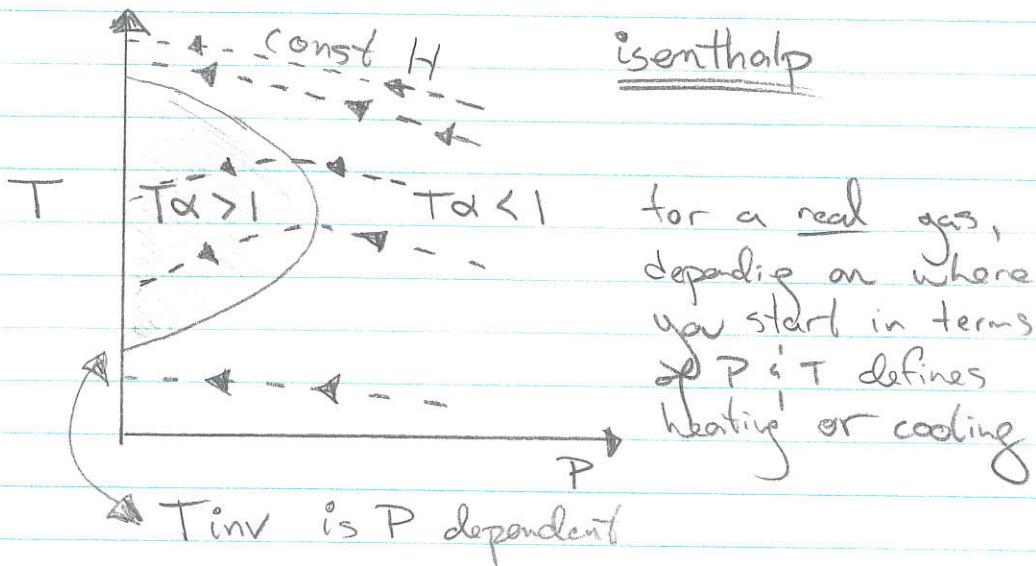
$T\alpha > 1$ decrease in pressure means $T \downarrow$

$$dP = -ve, (+ve)(-ve) = -ve$$

$T\alpha < 1$ decrease in pressure means $T \uparrow$

$$dP = -ve, (-ve)(-ve) = +ve$$

$T_{inv} = 1$, Joule-Thompson inversion Temperature



$$\begin{aligned} \text{max}(T_{inv}) \Rightarrow Xe &= 1486 \text{ K}, 161 \text{ K} = \text{boil} \\ O_2 &= 764 \text{ K}, 90 \text{ K} = \text{boil} \\ H_2 &= 204 \text{ K}, 20 \text{ K} = \text{boil} \end{aligned}$$

Note, for ideal gas, since $\alpha = 1/T$, no inversion

19-9

What about two at once?

$$T \notin P$$

$G(T, P, N)$ ← Gibbs free energy

$$dG = -SdT + VdP + \mu dN$$

$$\left. \frac{\partial G}{\partial T} \right|_{P, N} = -S = S(T, N, P)$$

$$\left. \frac{\partial G}{\partial P} \right|_{T, N} = V = V(T, P, N)$$

$$\left. \frac{\partial G}{\partial N} \right|_{T, V} = \mu = \mu(T, P, N)$$

* Know how to derive
(Assignment)

→ Where is this useful?

constant temperature

20-1

Last lecture: We concluded our discussion of thermodynamic potentials. We saw that depending on how you do an experiment, different qualities are held fixed (e.g. temperature, pressure, both etc). Depending on what is constrained, we must use different thermodynamic potentials.

Your textbook goes on to prove that for each TDP, equilibrium is at the minimum. (Only \bar{W} entropy do we maximize)

These experiments are not unrelated however, and properties determined in one can predict outcomes in others. This is done through Maxwell relations.

Recall:

$$dH = TdS + VdP$$

$$\left. \frac{\partial H}{\partial T} \right|_P = T \left. \frac{\partial S}{\partial T} \right|_P + \cancel{V \left. \frac{\partial P}{\partial T} \right|_R}$$

$$= T \left. \frac{\partial S}{\partial T} \right|_P$$

$$\left. \frac{\partial H}{\partial P} \right|_T = T \left. \frac{\partial S}{\partial P} \right|_T + V \left. \frac{\partial P}{\partial T} \right|_T$$

$$= T \left. \frac{\partial S}{\partial P} \right|_T + V$$

Then without proof, I said $T \left. \frac{\partial S}{\partial T} \right|_P = Nc_p$

$$= \frac{\partial}{\partial V} [T]_{S,N}$$

$$= \left. \frac{\partial T}{\partial V} \right|_{S,N}$$

so $\left. \frac{\partial T}{\partial V} \right|_{S,N} = - \left. \frac{\partial P}{\partial S} \right|_{V,N}$ Maxwell Relation

There are 21 for a single component, simple system.

Note these are different experiments, with equilibrium defined by different thermodynamic potentials.

Is there always a single Maxwell relation?

$$\text{No: } \left. \frac{\partial S}{\partial T} \right|_P = \frac{N C_P}{T}$$

What about $\left. \frac{\partial \mu}{\partial V} \right|_{T,N}$? Maybe.

We need an algorithm

① Look at the variables on the "bottom"

$$V, T, N$$

② Is there a TD potential which these are the natural variables of. Yes $F = F(T, V, N)$

$$C_P = \frac{I}{N} \left. \frac{\partial S}{\partial T} \right|_{P,N} = - \frac{I}{N} \left. \frac{\partial^2 G}{\partial T^2} \right|_P$$

Note the symmetry wrt Gibbs. All three are 2nd derivatives in T, P . This is why they are used as the standard basis

Now for another algorithm (to avoid going in circles). Recall

$$\left. \frac{\partial x}{\partial y} \right|_{f,z} = \frac{1}{\left. \frac{\partial y}{\partial x} \right|_{f,z}}$$

$$\left. \frac{\partial y}{\partial x} \right|_{f,z} = \frac{\left. (\partial y / \partial t) \right|_{f,z}}{\left. (\partial x / \partial t) \right|_{f,z}}$$

$$\left. \frac{\partial y}{\partial x} \right|_{f,z} = - \frac{\left. (\partial f / \partial x) \right|_{y,z}}{\left. (\partial f / \partial y) \right|_{x,z}}$$

Rule 1: If the derivative contains any potentials, bring them one-by-one to the numerator and eliminate them in their differential form.

Example $\left. \frac{\partial P}{\partial U} \right|_{T,N} = ?$

↑
this is a potential

so, $\left. \frac{\partial P}{\partial U} \right|_{T,N} = \frac{1}{\left. \frac{\partial U}{\partial P} \right|_{T,N}}$

21-1

28 March 2013 Last lecture, we began
in a discussion of MR. These partial
derivatives are 2nd derivatives of TD
potentials. They relate different experiments
to one another. We saw in some cases
there is a one-to-one mapping.
(21 in fact). For others, we must reduce
the derivatives according to an algorithm
in order to avoid going in circles. Hopefully
you have not drawn too many circles...

[Assignment extension comment]

21-2

Rule 2: If a derivative contains the chemical potential, μ , bring it to the numerator and eliminate it with the Gibbs-Duhem relation. ($d\mu = -SdT + VdP$)

$$\text{Example : } \frac{\partial \mu}{\partial S} \Big|_{T,N} = \frac{1}{S} \left[-SdT + VdP \right] \Big|_{T,N}$$

$$\boxed{\frac{\partial \mu}{\partial S} \Big|_{T,N} = V \frac{\partial P}{\partial S} \Big|_{T,N}}$$

μ is no longer present.

Note if it's one of the constants, it can be brought first to the numerator as we did w/ thermodynamic potentials

Rule 3: If a derivative contains the entropy, bring it to the numerator. Check whether you can eliminate it with a Maxwell relation. If not, insert a derivative wrt T to get specific heat

$$\text{Example : } \frac{\partial S}{\partial P} \Big|_{T,N} = -\frac{\partial^2 G}{\partial P \partial T} = -\frac{\partial^2 G}{\partial T \partial P}$$

21-4

Rule 4: If the volume is involved in a derivative, bring it to the numerator and express it in terms of α and χ_T

$$\left. \frac{\partial T}{\partial P} \right|_{V,N} = ?$$

$$\left. \frac{\partial T}{\partial P} \right|_{V,N} = - \frac{(\partial V / \partial P)_{T,N}}{(\partial V / \partial T)_{P,N}} = \frac{\chi_T}{\alpha}$$

At this stage, we should have expressed any derivative in terms of α , χ_T , and C_p . Note that the specific heat at constant volume may be lurking around

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_{V,N}$$

To relate it to the fundamental three, we start with the entropy, writing it as

$$S = S(T, P, N)$$

Then taking the full derivative

$$dS = \left. \frac{\partial S}{\partial T} \right|_{P,N} dT + \left. \frac{\partial S}{\partial P} \right|_{T,N} dP + \left. \frac{\partial S}{\partial N} \right|_{T,P} dN$$

21-6

Let's see what these are useful for

Consider adiabatic compression. T vs P?

$$\left. \frac{\partial T}{\partial P} \right|_{S,N} = -\left(\frac{\partial S}{\partial P} \right)_{T,N} = T \frac{V}{N} \frac{\alpha}{C_p}$$

MR

↑
specific
heat

↑
slope

↑
functional
form

What about the volume change?

$$\left. \frac{\partial V}{\partial P} \right|_{S,N} \xrightarrow{\text{define}} \kappa_s = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{S,N}$$

κ_s is adiabatic compressibility

$$\left. \frac{\partial V}{\partial P} \right|_{S,N} = -\frac{\left. \frac{\partial S}{\partial P} \right|_{V,N}}{\left. \frac{\partial S}{\partial V} \right|_{P,N}}$$

Insert a temperature derivative to top and bottom.

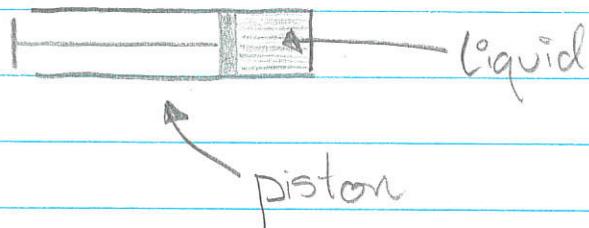
$$\text{i.e. } \left. \frac{\partial V}{\partial P} \right|_{S,N} = \frac{\left(-\left. \frac{\partial S}{\partial T} \right|_{V,N} \left. \frac{\partial T}{\partial P} \right|_{V,N} \right)}{\left(\left. \frac{\partial S}{\partial T} \right|_{P,N} \left. \frac{\partial T}{\partial V} \right|_{P,N} \right)}$$

22-1

Last lecture: We discussed the possibility of multiphase systems. There are basic questions which need to be addressed.

What decides whether a material is a solid, a liquid, or a gas? How does the transition occur? Are they always the same. Are multiphase mixtures stable (i.e. at equilibrium)?

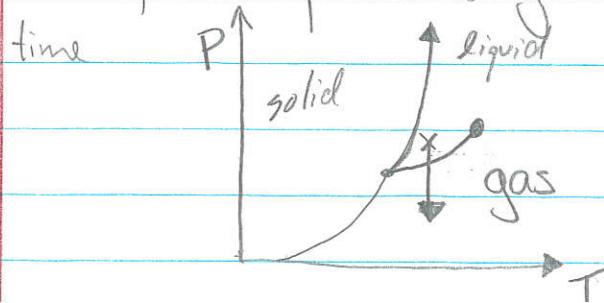
Let's start with an experiment:



This system starts out at some $P \text{, } T$

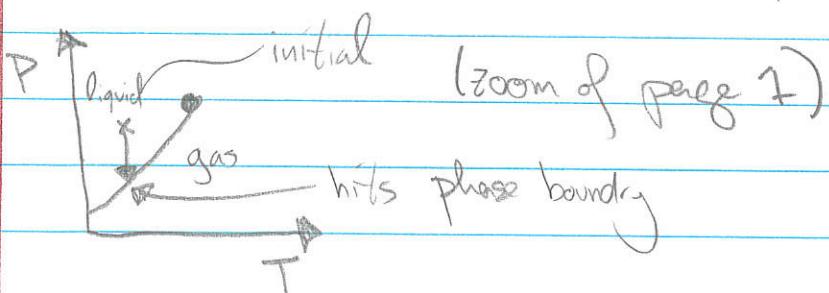
Let's now pull out the piston, increasing the volume at constant temperature (the container is diathermal)

Recall, the phase diagram we sketched last time



As much as we would like to think were strong, $P_{\text{initial}} \sim P_{\text{transition}}$, so you won't expand it much.

P drops until it hits the phase boundary



What can we saw thermodynamically at this point?

Note which variables are held constant
 T, P, N

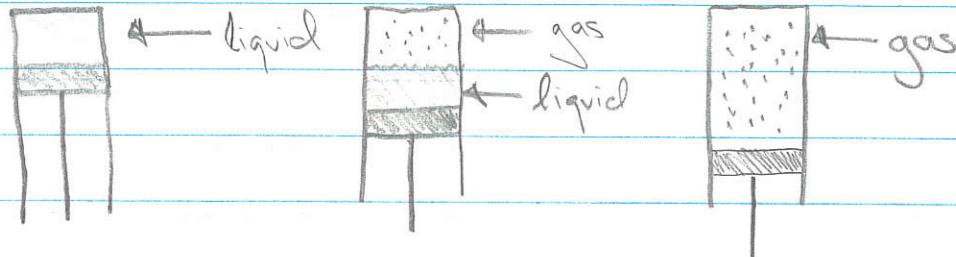
Thus the TD potential we must consider is the Gibbs free energy

A fundamental relation is valid \forall conditions, and describes the single, unique equilibrium state of the material. It is useful to think about a FR which is subject to the constraint of a specific phase.

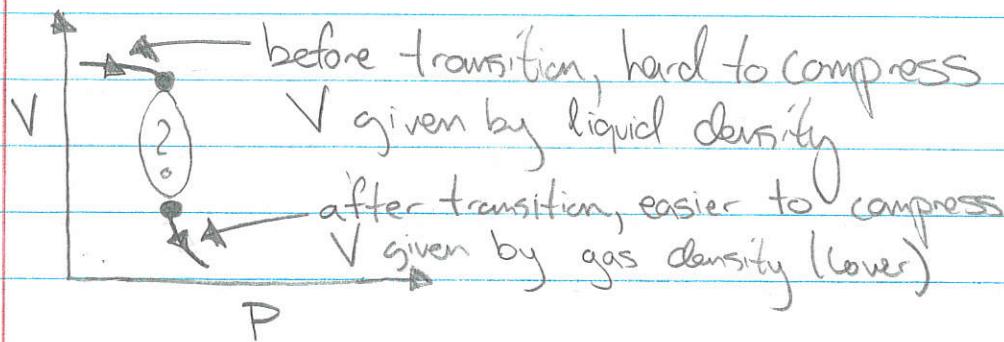
22-5

At the phase boundary, the Gibbs are equal. What is different? The density. Liquids are more dense than gases.

We observe two distinct phases



Aside: Since this is just one pure material, why can we even see a separation? Different phases have different chemical and physical properties, including optical properties



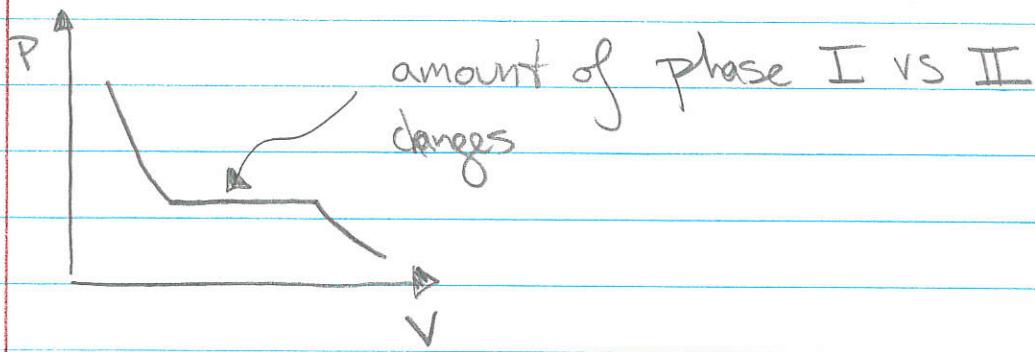
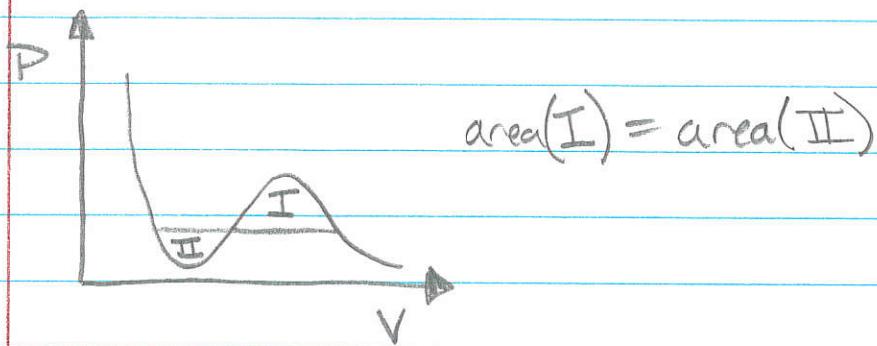
$$P_{\text{initial}} = \frac{N}{V_{\text{initial}}} \rightarrow P_{\text{final}} = \frac{N}{V_{\text{final}}}$$

↑ ↑

liquid final

22-7

Initially, $V \downarrow, P \uparrow$. It hits a point where $V \downarrow$ and $P \downarrow$. Mechanically unstable "vdW loop" (unphysical)
Maxwell showed



This is a sign of a discontinuous phase transition.

Equivalent to the statement "temperature does not change as water boils".

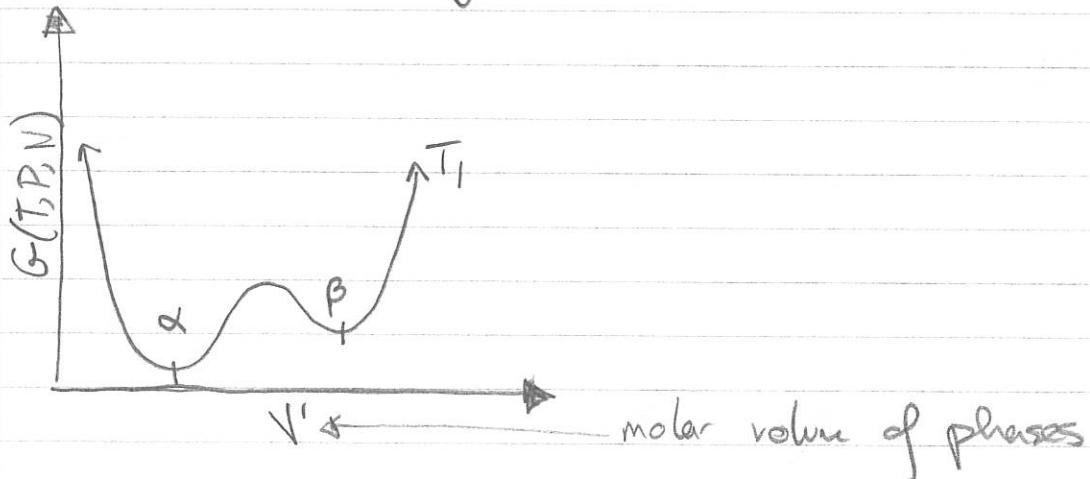
Returning to our sketch

Last lecture: We discussed two different types of phase transitions: continuous and discontinuous

The solid-liquid transition is an example of a discontinuous transition. The liquid-gas transition may be either, depending on where the critical point is

So far we have associated two features to a discontinuous transition: two phase coexistence and a flat region in the EOS. We will now discuss the third criteria (all are related)

Consider the following



α and β are both stable minima of G . If a thermal fluctuation occurs and it is small compared to the barrier, the system will relax back to its initial configuration. If it is large however (and some fluctuations always are), the system will hop either from $\alpha \rightarrow \beta$ or vice versa. One direction is easier than another, so α is considered the equilibrium state.

Two phase coexistence. $G_\alpha = G_\beta$

- ③ Above the transition temperature, the previously unfavoured phase is now preferred (relatively)

How does this happen?

$$G_\alpha = U_\alpha + P_\alpha V_\alpha - TS_\alpha$$

$$G_\beta = U_\beta + P_\beta V_\beta - TS_\beta$$

The temperature dependence of $U_\alpha(T) \neq U_\beta(T)$ and $P_\alpha(T) \neq P_\beta(T)$ and $S_\alpha(T) \neq S_\beta(T)$

So, even though at the transition

$G_\alpha(T_3) = G_\beta(T_3)$, the individual terms are not equal

Consider

$$G_\alpha = H_\alpha - TS_\alpha$$

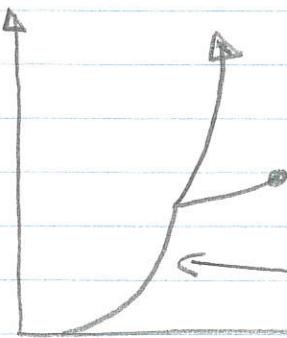
$$G_\beta = H_\beta - TS_\beta$$

if $G_\alpha = G_\beta$

$$H_\beta - H_\alpha = TS_\beta - TS_\alpha$$

$\Delta H = T\Delta S \leftarrow$ this quantity is known as the latent heat
 $= l$

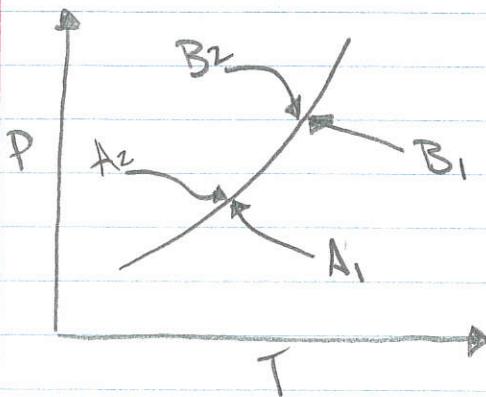
I have been drawing P-T diagrams like this



is there any significance to the slope?

Yes!

Consider



We know chemical potential are equal. Why?
They can go back and forth!

$$\mu_{A_2} = \mu_{A_1}$$

$$\text{and } \mu_{B_2} = \mu_{B_1}$$

$$\text{so } \mu_{B_2} - \mu_{A_2} = \mu_{B_1} - \mu_{A_1}$$

Recall Gibbs-Duhem $d\mu = -SdT + VdP$

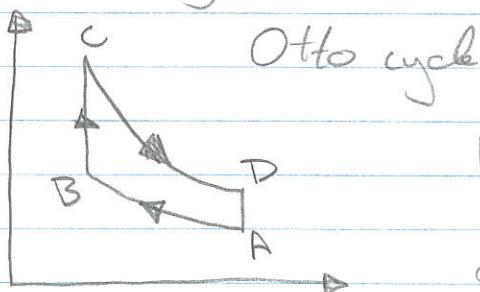
[#24 was shockwaves]

Review: Everything from the midterm (see lecture #12)

We looked at the maximum work theorem

We saw how engines can convert some fraction of heat into work. This conversion cannot occur completely. There is a maximum thermodynamic efficiency. This efficiency depends on the cycle of interest

We spent some time speaking about different engine cycles, specifically the diesel and Otto cycle



Note that we do work on the engine initially, and we get more back. Heat is involved!

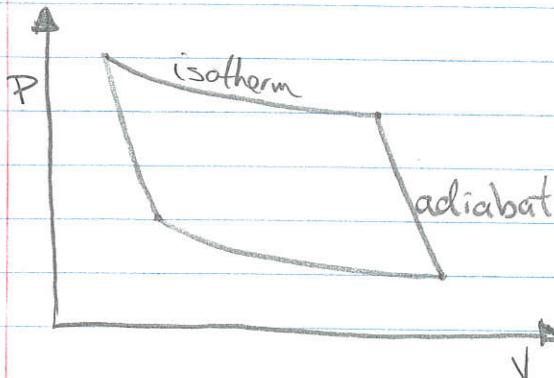
We found an efficiency of

$$\epsilon_{\text{Otto}} = 1 - \frac{1}{r^{1-1}}, \text{ where } r = \frac{V_A}{V_B}$$



This was the compression ratio

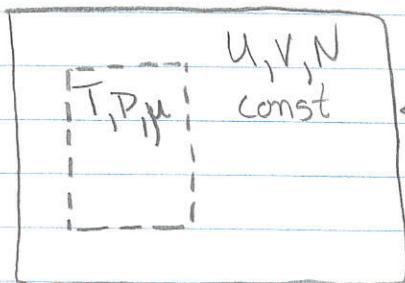
Recall the P-V diagram for the Carnot cycle



This is the most efficient way to extract work when two thermal baths are available

Next, we moved to a discussion of Legendre transformations. These we used to develop the thermodynamic potentials

TD potentials were used to explore the equilibrium properties of systems connected to reservoirs



the total system is subject to the familiar

We showed how to replace extensive variables \rightarrow intensive ones via the Legendre transforms to obtain new potentials

$$H = U + PV$$

Enthalpy

internal energy
Same as before

$$H = H(S, P, N)$$

Equilibrium when H min (assuming fixed S, P, N)

$$\text{We know } dU = TdS - PdV + \mu dN$$

$$\text{so } dF = \cancel{TdS} - PdV + \mu dN - SdT - TdS$$

$$dF = -SdT - PdV + \mu dN$$

$$\therefore \left. \frac{\partial F}{\partial T} \right|_{V,N} = -S \Leftrightarrow S = S(T, V, N)$$

$$\left. \frac{\partial F}{\partial V} \right|_{T,N} = -P \Leftrightarrow P = P(T, V, N)$$

$$\left. \frac{\partial F}{\partial N} \right|_{T,V} = \mu \Leftrightarrow \mu = \mu(T, V, N)$$

There are several of these, so be comfortable

It's also important to remember how these transforms work:

$$H = U + PV \Leftrightarrow \text{you need this in terms of } S, P, N$$

so an EOS will be involved

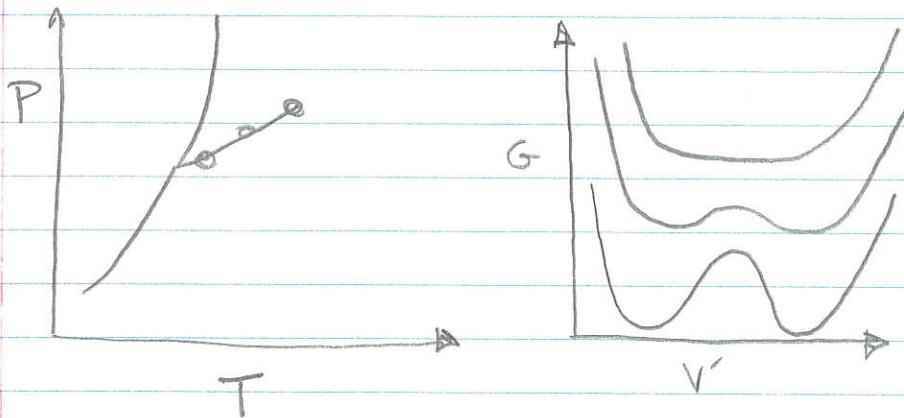
$$H = U(S, V, N) + PV(S, P, N)$$

\nwarrow to get rid of V , use $V(S, P, N)$
which is inverted form of EOS

Another system we discussed was the JT
throttling process

Although the Gibbs is equal for the two phases, they are not the same state. The entropy and enthalpy are different. To go between requires a latent heat.

Also recall



At some pt, there are no longer two minima. This leads to critical phenomena.

The final point we discussed was the slope of a phase boundary. It can be determined using the Clapeyron-Eqn

$$\frac{dP}{dT} = \frac{l}{T\Delta V}$$

recall that the latent heat is equal to the change in enthalpy, or $T\Delta S$

RTQ