

## Slide 1

Welcome everyone!

## Slide 2

### What is Entropy

- Entropy is a measure of a system's thermal energy per unit temperature that is unavailable for doing useful work, which is denoted by  $S$
- In simpler terms, entropy measures molecular disorder, or randomness, of a system. Basically, the messier a system is, the higher the entropy.
- The term and idea of entropy is coined by 1865 by the German physicist Rudolf Clausius
  - He is known for formulating the second law of thermodynamics (entropy in a closed system tends to increase)
  - He also provided a theoretical framework that explained translational, rotational, and vibrational molecular motion (we are not going to explore today)
- Here is an example of a messy draw, and because it is not organized, the system has a high entropy

## Slide 3

### Candy Example

- Here we have a beaker of candy, very organized, you can clearly see the separation of the two different colored candies.
- If we cover the beaker with one of our hands, and shake it really hard for about a min, what will we get?
- We will end up getting a beaker of mixed candies. There is clear separation between the red and white candies anymore.
- Now, let's think about this. Is it possible to go backwards to the beaker of organized candy in a min? No, you would need to pour the candy out and put the white ones back first and then the red ones
- It is much simpler to make something disorganized than to organized something
  - This is an example of the universe tend towards maximum entropy
  - Much easier to keep something messy

## Slide 4

### Entropy of Water

- Let think about entropy in a molecular scale, keeping the candy example in mind
- Here we have some ice cubes
  - On a molecular level, this is the structure of the ice cube
  - All the water molecules are close together, very organized
- What would happen if we heat up the ice cubes?
  - We will have a puddle of water
  - On a molecular level, the water molecules are not stationary anymore. They are free to move within the liquid, but they cannot move in the air
- Now, what would happen if we heated the liquid up?
  - We will have water vapor, like the steam we will get if we boil water.

- Now, can someone tell me what gas looks like on a molecular level? They are free to move wherever they want, just within the boundaries of a system

#### Slide 5

##### Enthalpy

- Enthalpy is the sum of the internal energy and the product of the pressure and volume of a thermodynamics system, which is told by the equation  $H = U + PV$
- It basically informs us about how much heat is in a system
- The idea and word were coined by the Dutch scientist Heike Kamerlingh Onnes in 1909
  - One of the coolest thing he discovered was that the electrical resistance of mercury completely disappeared at temperatures a few degrees above absolute zero (Not going to get into today, just something cool)
- So basically, if a system is absorbing heat, enthalpy is increasing. If a system is releasing heat, the enthalpy is decreasing

#### Slide 6

##### Change in Enthalpy

- Let's use cooking tea as an example of enthalpy
- Can someone remind me what are the factors that contribute to enthalpy?
  - Pressure, Volume, and temperature
- If we are heating something up, it is good to know the heat capacity
  - Heat capacity is the heat required to be absorbed by an object for a temperature change
  - Let's assume the heat capacity of tea is about the same as water

#### Slide 7

##### Change in Enthalpy

- So if we are cooking tea from 25°C to 100°C, and we close the heat the moment tea starts to boil. We assume there is not much loss of tea.
- The tea is constantly exposed to air, so the pressure during the process did not change.
- The only variable that change during the process is temperature
- Let do so math to calculate how much energy is needed to heat up 500 g of tea

#### Slide 8

##### Change in Enthalpy

- Here it is
- Because we assumed that pressure and volume is the same throughout the process of cooking tea, we only need to take care of the change in temperature
- Here we have mass of tea \* the heat capacity \* diff in temperature
- Plug in all the values
- We will need 156750 joules to boil 500g of tea from 25°C to 100°C

#### Slide 9

##### Gibbs free energy

- Gibbs free energy is used to calculate the maximum amount of work that may be performed by a thermodynamically closed system
- It is developed in the 1870s by Gibbs
  - He was known for his significant theoretical contributions to physics, chemistry and mathematics (not going to get into today)

#### Slide 10

##### Gibbs Example

- Let me use myself as an example
- In the morning, I am fully charged, very excited to do anything. My gibbs free energy is very high, willing to do a lot of work (work refers to anything that requires energy)
- As the day progresses, I cook food, read some book, play some games, my battery starts to slowly decrease
- At the end of the day, I am exhausted. Barely have enough energy to stay awake. I don't have any more energy that allows me to do more work

#### Slide 11

##### Spontaneity

- One very important thing gibbs free energy tell us is the spontaneity of a certain process
- The change in gibbs free energy tell is whether or not a process occur without any external input to the system
- The change in Gibbs free energy can be calculated by  $\Delta H - T\Delta S$ 
  - Does anyone remember what is H and S
  - the change in enthalpy minus the temperature \* the change in entropy
- So how does gibbs free energy tell us about spontaneity
  - $\Delta G < 0$  Spontaneous
  - $\Delta G = 0$  Equilibrium
  - $\Delta G > 0$  Non-Spontaneous

#### Slide 12

##### Rock Example

- If we put a rock on a downhill
  - Do you think the rock would be more willing to roll down or up?
  - Which one does not required you to put in energy to make it happen
- If you want the rock to roll uphill, you would have to push the rock up, which requires you to put in energy.  $\Delta G > 0$ . It does not happen on its own

#### Slide 13

##### Thermodynamics Equilibrium

- Equilibrium happens when a system have no tendency to change any of its properties spontaneously
- You can think of it as these rock, all balanced
- If you change the size of any rock, or the shape of the rocks, the system is not balanced anymore. Other rocks will need to change too to keep the system balance

## Slide 14

### Swimming

- Let's use swimming as an example
- On a hot summer day, you really want to go swimming
- You get to the pool and you realized the pool is filled with people that also want to swim on this hot summer day
- To make sure everyone has enough space to swim happily, you decided to expand the swimming pool. You magically did it!
- Now the equilibrium of the system is broken, the size of the swimming pool has doubled? What do you think would happen?
- People would start moving over to the other side of the pool
- And eventually, there will be about the same amount of people at both side of the pool
- A new equilibrium had reached.
  - It is less crowded, everyone has enough space to swim happily
  - And let's hope there won't be more people that want to swim on this hot summer day, because you can't magically make another pool

Take a 5-10 min break!!!

Before jumping into more advance stuff

## Slide 15

### Phase Diagram

- Now we are getting into the more advance thing of today lecture
- Alfonso had showed a similar phase diagram last week, but it never hurts to review
- The lines are coexistence curves
  - The red solid line represents solid and gas phase exist at the same time in equilibrium
  - Changing the temperature or liquid by a bit would shift the entire system to either a solid or a gas
  - The green dashed line is the solid and liquid coexistence curve
  - The blue solid line is the liquid and gas coexistence curve
    - We are going to explore liquid and gas equilibrium in more detail later
- There are also two red points that are really important
  - The triple point is where solid, liquid and gas all exist in equilibrium
  - The critical point is the highest temperature and pressure where a pure material can exist in vapor/liquid equilibrium
  - Remember back to the molecular structure of liquid and gas
    - At such high temperatures, it is extremely difficult to differentiate between liquid and gas
    - Both phases are freely to move around, no define structure

## Slide 16

### Single Phase Vapor Liquid Equilibrium

- Here we have a system, where the liquid phase and the gas phase is in equilibrium with

each other

- What does that mean?
  - The temperature of the gas and liquid are equal, that's thermal equilibrium
  - The pressure exerted by the gas and liquid are equal, that's mechanical equilibrium
  - The gibbs energy of the gas and liquid are equal, that's chemical equilibrium
- The gas can still turn into liquid, and liquid can still turn into gas
  - But they change that the same time, so the amount of gas and liquid overall does not change
- Question: If you increase the pressure of the system, what would the new equilibrium look like?

#### Slide 17

##### Single Phase Vapor Liquid Equilibrium

- Increasing the pressure means that you are pushing down on the piston more
- The total volume that the liquid and gas can occupy decreases
  - That means there would be more liquid and less gas at the new equilibrium
- Liquid takes us less space than gas, so to avoid being too crowded, molecules would prefer to be in liquid phase

#### Slide 18

##### Bubble Line

- We had been talking about single phase equilibrium, now let's talk a look at two component vapor liquid equilibrium
- We are going to derive a two component liquid and vapor phase diagram
- Let's consider a system where you have component A and B
  - Component A is volatile (evaporates very easily, water)
  - Component B is non-volatile (doesn't evaporates that easily)
- That means as I increase the temperature of the system, only component A would vaporized
- Let's graph Pressure vs mole fraction of B using Raoult's Law
  - When there is only component A in the liquid phase, the pressure would be the vapor pressure of pure component A
  - As component A slowly decreases, the pressure of the system would also decrease, eventually reach 0

#### Slide 19

##### Bubble Line

- Now using the same logic, but this time component B is volatile
- And we do the same thing, graphing pressure vs mole fraction using raoult's law
- We will have something similar
  - No pressure when there is no component B, and the vapor pressure of pure component B when there's only B
- Now we connect  $P^*_A$  to  $P^*_B$ , that is our bubble line

- Bubble line is the pressure at a given temperature where the first bubble of vapor will form. The end point of vapor liquid equilibrium, above the bubble line would be pure liquid

#### Slide 20

- We can do something similar to get a dew line, but this time we are unable to simplify the scenario
- Therefore, we have to go through some math
  - Not going to get into detail, but if interested, we can discuss another time
- The only important thing we got out of that math, is an equation for our dew line
  - The pressure at a given temperature where the first drop of liquid is formed
- Now we put both the bubble and dew line together, we get the vapor liquid phase diagram for a two component system

#### Slide 21

- Now let's label the graph, and see which section is liquid and which section is vapor
- Above the bubble line, we have pure vapor
- As we decrease pressure, we will react the region between the two line
  - Which is the region where vapor and liquid coexist in equilibrium
  - Different from the phase diagram I showed a few slides before, the region of coexistence is much bigger.
- And as you decrease pressure more, you would have gas below the dew line

#### Slide 22

- Here is a similar graph that tell us about vapor liquid equilibrium of a two component system
- However, this time we keep pressure constant rather than temperature
  - Realistically, keeping pressure constant is more do-able than keeping temperature constant