

Free Energy + Equilibrium

Second Law: Total entropy of Universe will increase

- For an isolated system, equilibrium is at S_{\max}
- What if our system isn't isolated?
It can exchange energy w/ environment

Assume environment is an infinite reservoir (its T doesn't change)

Then $\Delta S_{\text{tot}} = \Delta S + \Delta S_R$

$$dS_{\text{tot}} = dS + dS_R$$

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

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

$$dS_{\text{tot}} = dS + \frac{1}{T_R}dU_R + \frac{P_R}{T_R}dV_R - \frac{\mu_R}{T_R}dN_R$$

Assume V, N are fixed (exchange only heat)

$$\text{Then } dV = dV_R = 0$$

$$dN = dN_R = 0$$

$$dS_{\text{tot}} = dS + \frac{1}{T_R} dU_e$$

$$T_R = T, dU_e = -dU$$

$$\begin{aligned} dS_{\text{tot}} &= dS - \frac{1}{T} dU \\ &= -\frac{1}{T} (dU - T dS) = -\frac{1}{T} dF \end{aligned}$$

$$\Delta S_{\text{tot}} \propto -\Delta F$$

System will evolve towards minimal F

($-\Delta F$ pros are favored)

S_{tot} will increase

F_{sys} will decrease

- Similar to potential energy U

② const $T + V$, $\Delta F < 0$ indicates a spontaneous process

Similar for G

const P, T

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV$$

$$dS_{\text{tot}} = -\frac{1}{T} dG$$

Summary:

constant N and

$$U, V: \Delta S > 0$$

$$T, V: \Delta F < 0$$

$$P, T: \Delta G < 0$$

Intuition



$$F = U - TS \quad \begin{matrix} \text{Can exchange only} \\ \text{heat} \end{matrix}$$

at const T ,

$$\Delta F = \Delta U - T\Delta S$$

$\Delta F < 0$ happens when the system loses energy + gains entropy

isothermal systems which don't do work try to minimize energy while maximizing entropy

The system can gain energy spontaneously, as long as $T\Delta S > \Delta U$

Now:

$$G = U + PV - TS$$

System can exchange heat + Volume

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{Const } T, P$$

System minimizes $U + PV$ while increasing S

Example: Falling object

- During fall, $\Delta U = 0$ (potential is converted to kinetic)
- When object lands, extra energy is transferred to surroundings as heat, sound

This lowers U of the object

- It also lowers S of the object
- Not all energy will leave object
- Energy transfer until $\Delta U + T\Delta S$ balance

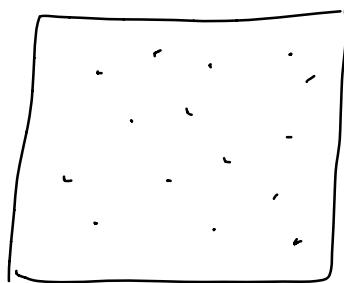
Extensive vs Intensive

We've discussed many different variables now:-

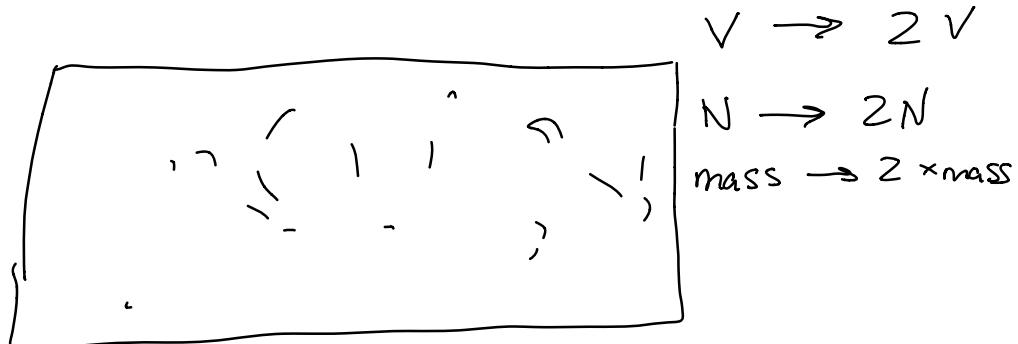
$U, V, N, S, T, P, \mu, H, F, G, \dots$

One useful way to organize:

If I change the amount of matter/size in my system, which variables change with it?



$P, T, V, U, \text{etc..}$



$$U? \quad U \approx \frac{1}{2}mv^2 \times N$$

$$U \rightarrow zU$$

$$S \rightarrow zS$$

$$\rho \text{ (density)} \quad \rho = \frac{m}{v} \rightarrow \frac{zm}{zv} = \rho$$

$$\rho \rightarrow \rho$$

$$T? \quad T \sim \frac{U}{N} \rightarrow \frac{zu}{zn} = \frac{u}{n}$$

$$T \rightarrow T$$

$$P? \quad P \sim \frac{N\tau}{v} = \frac{ZN(\tau)}{Zv} = \frac{Z\tau}{v} = \varphi$$

$$P \rightarrow \varphi$$

$$U \rightarrow U$$

Additive: V, N, S, U, mass

Non Additive: T, P, S, μ

$$F = U - TS \rightarrow zU - zTS \rightarrow zF$$

F, G, H are additive

Extensive: V, N, S, U, H, F, G

Intensive: T, P, μ, S

$$\frac{(E_{ext})}{(E_{ext})} \rightarrow (int) \quad \frac{m}{V} \rightarrow S$$

$$(E_{ext})(int) \rightarrow (ext) \quad V \cdot g \rightarrow m$$

$$(E_{ext})(E_{ext}) \rightarrow ? \quad V \cdot V = V^2$$

$$(E_{ext}) + (E_{ext}) \rightarrow (ext)$$

$$(E_{ext}) + (int) \rightarrow ?$$

$$V + \frac{V}{N} \rightarrow ?$$

Consider:

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

Suppose I go from $N \rightarrow zN$
while T, P don't change

$$\mu \rightarrow \mu$$

$$G \rightarrow zG$$

$$N \rightarrow zN \quad \frac{\Delta G}{\Delta N} = \frac{G}{z} = \mu$$

$$\mu = \frac{G}{N}$$

$$G = N\mu$$

μ : is the Gibbs energy per particle

$G = \max$ non-PV work

$$\mu = \frac{G}{N}$$

Ideal Gas: $T \propto \frac{U}{N}$ total E per particle

$$\mu = \frac{G}{N} \quad \begin{matrix} \text{total available non-PV work} \\ \text{per particle} \end{matrix}$$

An important consequence: phase transitions

Consider the transition from water to gas

Under what circumstances will it happen?

$$\Delta G_{e \rightarrow g} = \Delta H_{e \rightarrow g} - T \Delta S_{e \rightarrow g}$$

ΔH is the energy required to:

- Overcome intermolecular forces
- Increase the volume of the substance
(work against the atmosphere)

- Balance between energy minimization
+
Entropy maximization
- To transform a liquid to a gas, we must raise its energy
- A gas has more microstates than a liquid $S >$ (higher)
- Transition will occur automatically if

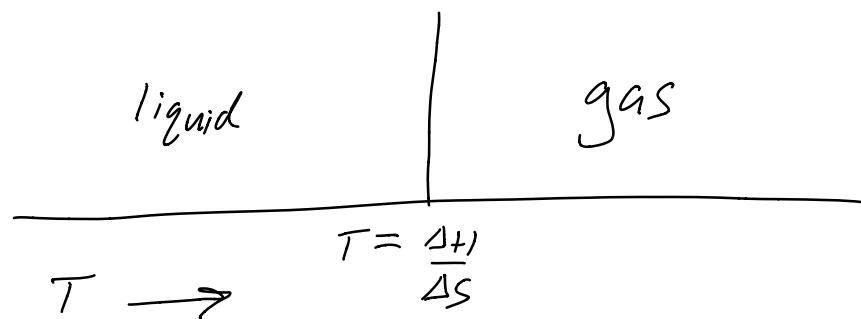
$$\Delta G_{l \rightarrow g} < 0$$

$$\Delta H_{l \rightarrow g} < T \Delta S_{l \rightarrow g}$$

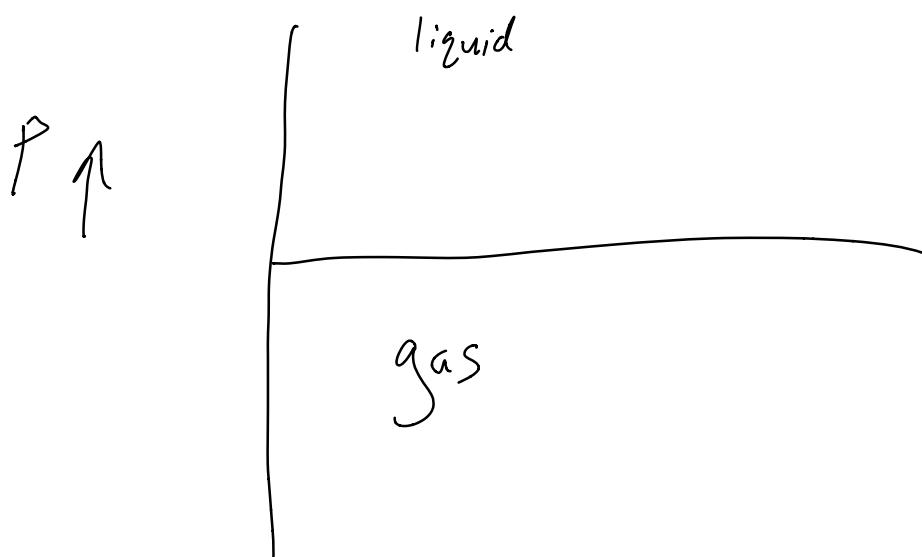
"Vaporization occurs spontaneously if the energy required is less than the entropy created"

$\Delta H + \Delta S$ are not very temp dependent

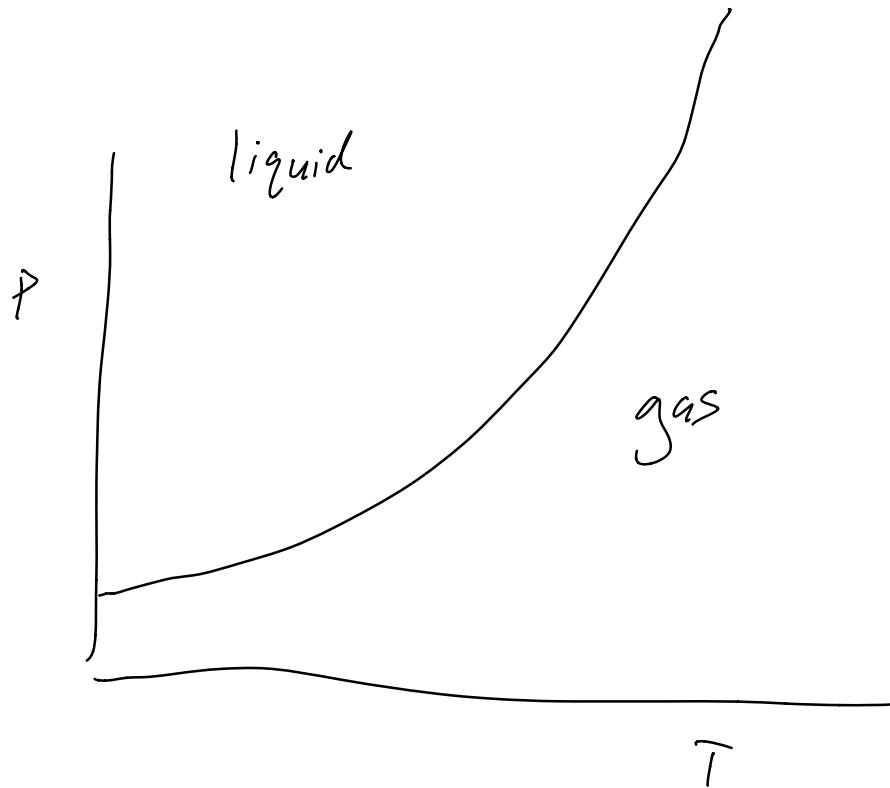
if $T > \frac{\Delta H}{\Delta S}$, water will vaporize



$\Delta H + \Delta S$ ARE dependent on pressure



Putting them together

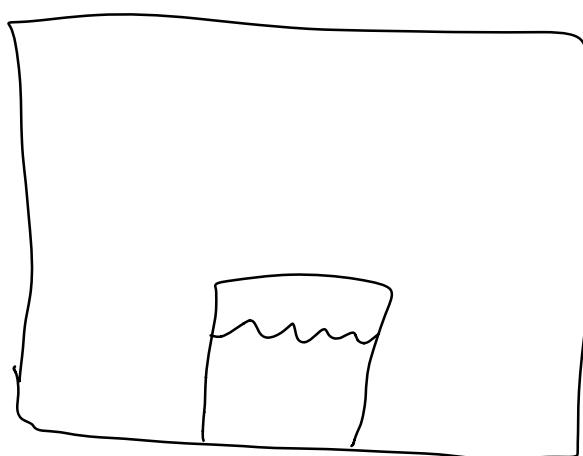


if I have a glass of water in a closed chamber

if (T, P) is above that curve, will stay

liquid

else, will
evaporate



The line separating phases is the phase boundary

- Along this line, both phases can coexist in equilibrium

$$\text{i.e. } G_e = G_g \quad (\Delta G = 0)$$

$$\text{at } T, P, \quad G_e = G_g$$

also true at some point $T + dT, P + dP$

$$dG_e = dG_g \quad dG = -SdT + VdP + \mu dN$$

$$-S_e dT + V_e dP = -S_g dT + V_g dP \\ (dN = 0)$$

Therefore:

$$\frac{dP}{dT} = \frac{S_g - S_e}{V_g - V_e}$$

slope of the boundary curve

$$\frac{dP}{dT} = \frac{\Delta S_{l \rightarrow g}}{\Delta V_{l \rightarrow g}}$$

$$\Delta S = \frac{Q}{T}$$

$$\Delta S_{l \rightarrow g} = \frac{m L}{T}$$

$$\frac{dP}{dT} = \frac{m L}{T \Delta V}$$

Clausius-Clapeyron relation

Differential Eqn for phase boundary on a
PT diagram

Ex: Consider the transition from liquid to gas:

Assume: L does not vary with T

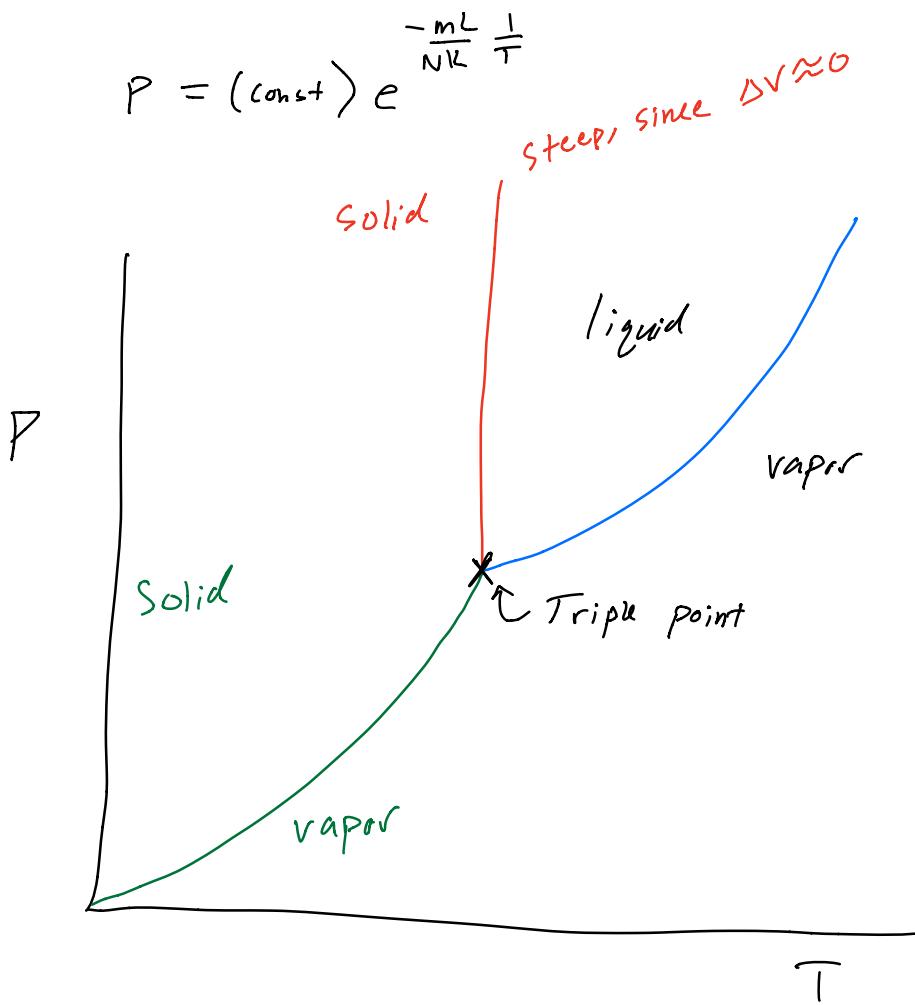
$$V_g \gg V_l \quad (\Delta V \rightarrow V_g - V_l = V)$$

$$\frac{dP}{dT} = \frac{m L}{T V} \quad V = \frac{N k T}{P}$$

$$\frac{dP}{dT} = \frac{mL}{T \left(\frac{NkT}{P} \right)} = \frac{mL}{Nk} \frac{P}{T^2}$$

$$\frac{dP}{P} = \frac{mL}{Nk} \frac{dT}{T^2}$$

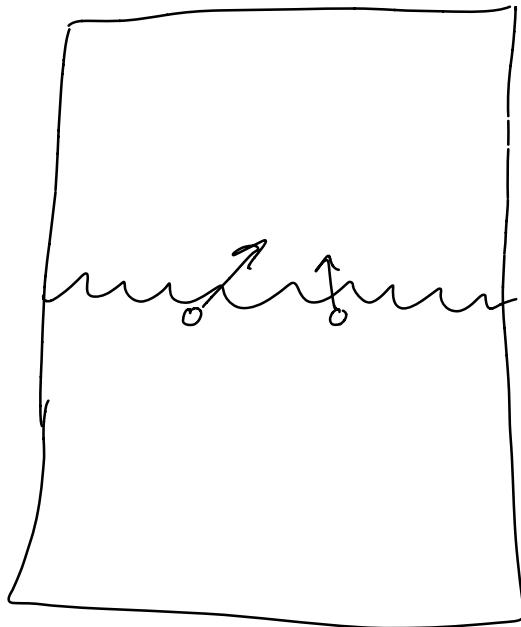
$$\ln(P) = -\frac{mL}{Nk} \frac{1}{T} + \text{const}$$



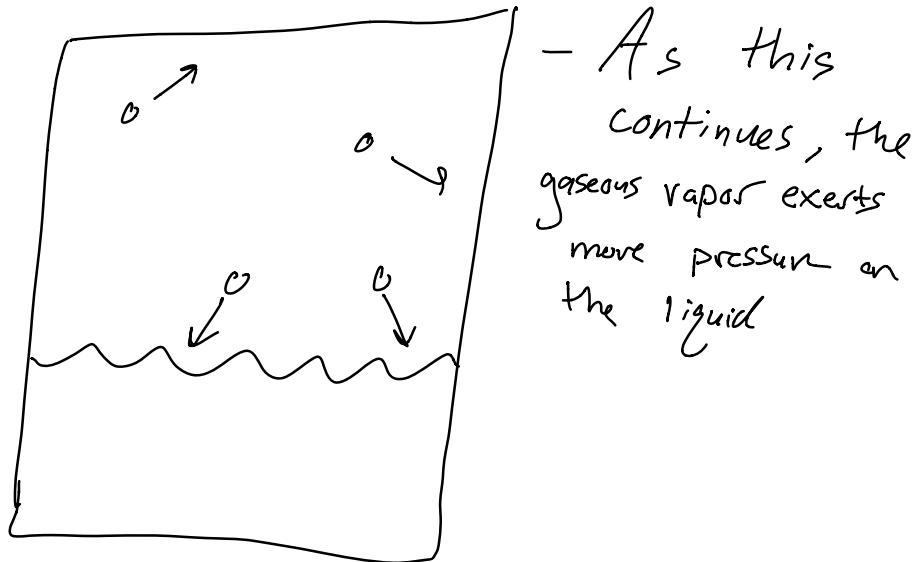
Triple point: all 3 phases exist in equilibrium

The "P" in the above is the vapor pressure: The pressure exerted by the vapor hovering above its condensed state in equilibrium

Ex:



- If I increase the temp, some liquid molecules @ the surface get enough energy to join the gas



- Some of these gas molecules will re-condense into the liquid

Every second, a certain number of liquid turns to gas, and a certain number of gas turns to liquid

Eventually, these rates will equal (equilibrium)

- Pressure of the vapor when this happens is the "vapor pressure"

(If you placed a cup of water in a sealed container, it will evaporate until it reaches this equilibrium)

- What matters is the pressure exerted by water vapor, not air or other molecules

In a mixture of many^{ideal} gases the total pressure is equal to the sum of the partial pressure of each species

$$P = P_A + P_B + P_C + \dots$$

Dalton's Law

- Liquid water only "feels" pressure from water vapor, not all of the air

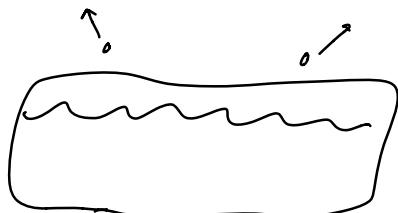
- Evaporation is normally spontaneous, even below 100°C , because the partial pressure of water vapor in the air is below equilibrium

- This is what humidity is: the ratio of current pressure of water vapor to its equilibrium vapor pressure

when $H = 100\%$, no more evaporation

Consider a pot of water on the stove
(no lid)

1) Don't turn stove on



- Pressure of water vapor is low
 - molecules toward the surface will leave + join the gas
 - This doesn't alter the pressure
 - water level slowly depletes into gas

2) Add heat to the water

- molecules leave the surface \oplus faster rate
- At high enough temp, the new vapor molecules exert upward pressure against the atmospheric air molecules
 - This reduces the pressure pushing down on the liquid
- At a high enough temp, the pressure of evaporated molecules is enough to cancel the atmospheric pressure
- Now, even water molecules at the bottom of the pan can become gaseous, forming bubbles which rise to the surface
 - This is called boiling

Boiling point: vapor pressure = exterior pressure

For water, $P(T) = 1 \text{ atm } \oplus 100^\circ\text{C}$

This is why it's easier to boil water \oplus higher altitudes