Lecture 14, Oct 11, 2022

Gibbs-Duhem Equation

- How do we evaluate g in terms of known quantities?
  - We want $g(T, P)$ because in the end these are the only things we can directly measure
- $G = H - TS = U + PV - TS \implies \mathrm{d}G = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T$
  - Using the Gibbs equation $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + g\mathrm{d}m$ and substitute this in
  - $\mathrm{d}G = T\mathrm{d}S - P\mathrm{d}V + g\mathrm{d}m + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T = g\mathrm{d}m + V\mathrm{d}P - S\mathrm{d}T$
  - Since $G = gm \implies \mathrm{d}G = g\mathrm{d}m + m\mathrm{d}g \implies g\mathrm{d}m + m\mathrm{d}g = g\mathrm{d}m + V\mathrm{d}P - S\mathrm{d}T$
  - $m\mathrm{d}g = V\mathrm{d}P - S\mathrm{d}T \implies \mathrm{d}g = v\mathrm{d}P - s\mathrm{d}P$, known as the Gibbs-Duhem Equation

Definition

The Gibbs-Duhem Equation: $\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T$

Phase Equilibrium

- Intuitively as we heat the system the pressure should increase
  - Plotting P vs T gives us a line; every point along this line is an equilibrium state
  - For every P_{sat} saturation pressure we have a corresponding saturation temperature T_{sat}
  - Can we derive this line?
- At equilibrium $g_f = g_g$; suppose we change temperature by $\mathrm{d}T$ and pressure by $\mathrm{d}P$ and get a new equilibrium
  - At the new equilibrium $g_f + \mathrm{d}g_f = g_g + \mathrm{d}g_g \implies \mathrm{d}g_f = \mathrm{d}g_g$
  - Using the Gibbs-Duhem equation: $v_f\mathrm{d}P - s_f\mathrm{d}T = v_g\mathrm{d}P - s_g\mathrm{d}T$
    - Note $\mathrm{d}P$ and $\mathrm{d}T$ are the same for the liquid and gas
  - $\dfrac{\mathrm{d}P}{\mathrm{d}T} = \dfrac{s_g - s_f}{v_g - v_f}$ is the slope of our P-T curve, however s_f, s_g are hard to determine
    - It's easier to work with h because it's the latent heat, which can be looked up
- We now want a relationship between h and s
  - $h = u + Pv \implies \mathrm{d}h = \mathrm{d}u + P\mathrm{d}v + v\mathrm{d}P$
  - Using the Gibbs equation: $T\mathrm{d}s = \mathrm{d}u + P\mathrm{d}v \implies \mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$
  - Since the system is in equilibrium, $\mathrm{d}P = \mathrm{d}v = 0$ and $\mathrm{d}h = T\mathrm{d}s, T = T_{sat}, P = P_{sat}$
  - $\mathrm{d}s = \dfrac{\mathrm{d}h}{T} \implies s_2 - s_1 = \displaystyle\int \dfrac{\mathrm{d}h}{T} = \dfrac{h_2 - h_1}{T}$ since T is a constant
    - This makes sense because $Q_{12} = h_2 - h_1$, because entropy generation in this system can only be due to heat added, which goes directly to enthalpy

Definition

The latent heat of vaporization $h_{fg} = h_g - h_f$

This can be looked up in a table for specific substances

Definition

The Clapeyron Equation (applies to any two phases): $\dfrac{\mathrm{d}P}{\mathrm{d}T} = \dfrac{h_{fg}}{T(v_g - v_f)}$

- Note we never made any assumptions about the phases, so this equation applies for any two phases (e.g. liquid-solid, gas-solid)

Liquid-Vapour Equilibrium

- If we assume that this is a liquid and gas, then we can assume $v_f \ll v_g$
- Also assume the vapour is an ideal gas, so $v_g = \dfrac{RT}{P}$
- Putting this back into the equation we get $\dfrac{\mathrm{d}P}{\mathrm{d}T} = \dfrac{h_{fg}P}{RT^2}$
- Assume h_{fg} is constant, then $\displaystyle\int \frac{\mathrm{d}P}{P} = \frac{h_{fg}}{R}\int \frac{\mathrm{d}T}{T^2}$
- $\ln P = -\dfrac{h_{fg}}{RT} + C$ is the Clausius-Clapeyron Equation

Definition

The Clausius-Clapeyron Equation (only applies for liquid-vapour systems): $\ln P = -\dfrac{h_{fg}}{RT} + C$

- This means $P_{sat} = c\exp\left(-\dfrac{h_{fg}}{RT_{sat}}\right)$
- If we know one state, we can calculate the entire curve
  - e.g. for water at $P_{sat} = 1\text{atm}$, $T_{sat} = 100°\text{C}$, so we can calculate c to get the entire curve
- Example: in a pressure cooker P_{sat} is high, so T_{sat} is also high and cooks the food faster

Solid-Liquid Equilibrium

- Denote solid phase by subscript s, so $\dfrac{\mathrm{d}P}{\mathrm{d}T} = \dfrac{h_{sf}}{T(v_f - v_s)}$ where h_{sf} is the latent heat of fusion
  - Is this slope greater or less than zero?
  - $v_f - v_s$ is the only thing that can be negative
- Suppose we have a liquid and we put a solid in it, which sinks to the bottom, then $\rho_s > \rho_f \implies v_s < v_f$ and $v_f - v_s > 0$
  - For most solids, they are denser than their liquid counterparts, so $\dfrac{\mathrm{d}P}{\mathrm{d}T} > 0$
- One big exception is water, which has $\rho_f > \rho_s \implies \dfrac{\mathrm{d}P}{\mathrm{d}T} < 0$
- For most solids, the separation between solid and liquid and liquid and vapour both have positive slopes on a P-T diagram
  - The solid-vapour boundary also has a positive slope
- We can have phase transitions across any of the 3 boundaries
- The point at which all 3 boundaries meet is the *triple point*, the point where liquid, solid, and vapour are in equilibrium
  - At the triple point, we can have boiling and freezing at the same time!

- For water this is at $(0.01°\text{C}, 61.73\text{Pa})$
- The triple point is *invariant*, so we can use it for calibration of instruments

- For water/ice, if we increase the pressure, the melting point decreases
  - This is why if we apply pressure on ice, the ice around that pressure point melts (regelation)
  - This is also how skates work
- If we want to dry something, we can either increase the temperature (oven drying), or decrease the pressure (vacuum drying)
  - However both of these methods don't work well for delicate things like cells
  - Freeze drying decreases the temperature first, and then decrease the pressure; the moisture sublimates directly and delicate structures are preserved due to the freezing

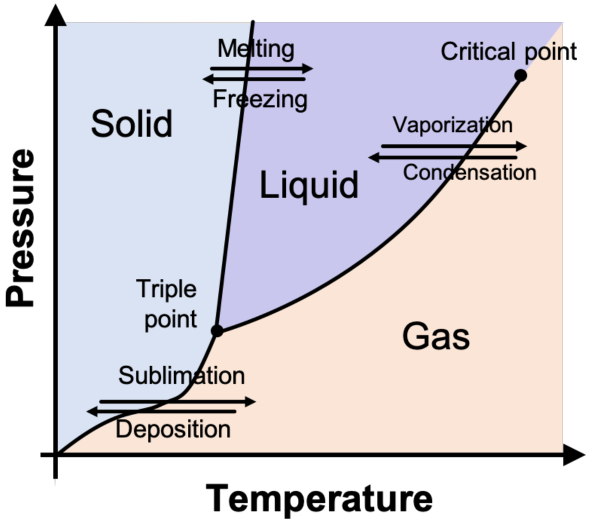

Figure 1: Phase diagram with triple point

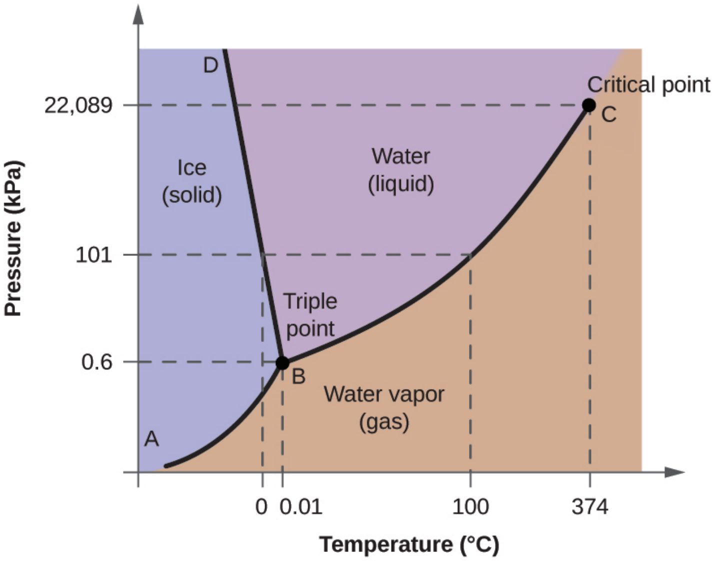

Figure 2: Phase diagram of water