

II.3 Classification of phase transitions

(second reading assignment)

Why is Gibbs free energy continuous?

all thermodynamic potentials are continuous within a phase. At transition:

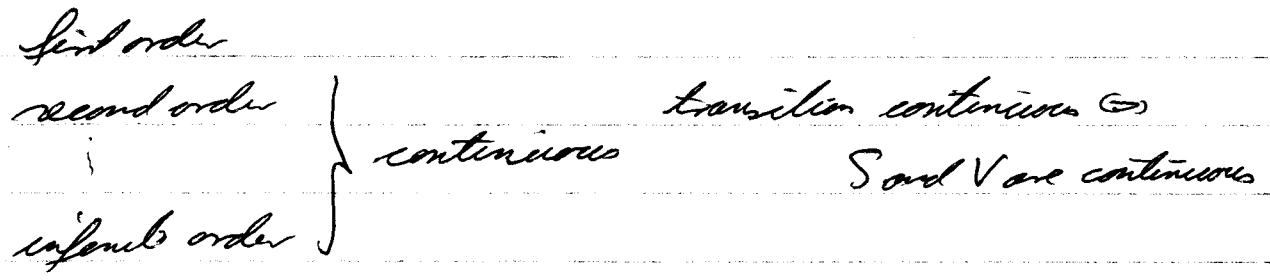
$$G = U - TS - XY = \sum_{i=1}^r n_i \mu_i$$

n_i constant μ_i continuous because of equilibrium cond.

$G(P, T, \{N_i\})$ intensive variables do not control how many particles are in which phase

A phase transition is a non-analyticity in the Gibbs free energy

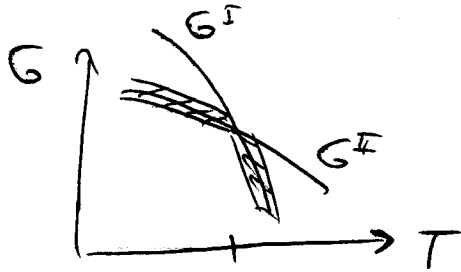
Continuous vs nth order transition:



example: PVT system

first-order transition

fixed P :



G decreases as a function of T

G is a concave function of T

$G^I = n\mu^I$ high temperature phase

$G^{II} = n\mu^{II}$ low temperature phase

$$G = \min\{G^I, G^{II}\} \Rightarrow G^I > G^{II} \text{ for } T < T_c$$

$$G^I < G^{II} \text{ for } T > T_c$$

$$\Rightarrow -\left(\frac{\partial G^I}{\partial T}\right)_{P, \{N_i\}} > -\left(\frac{\partial G^{II}}{\partial T}\right)_{P, \{N_i\}} \Rightarrow S^I > S^{II} \text{ (at } T_c)$$

$$\Rightarrow \text{jump in entropy} = \Delta S = S^I - S^{II}$$

\rightarrow jump in enthalpy $H = G + TS$:

$$\Delta H = H^I - H^{II} = T_c \Delta S \quad \text{"latent heat"}$$

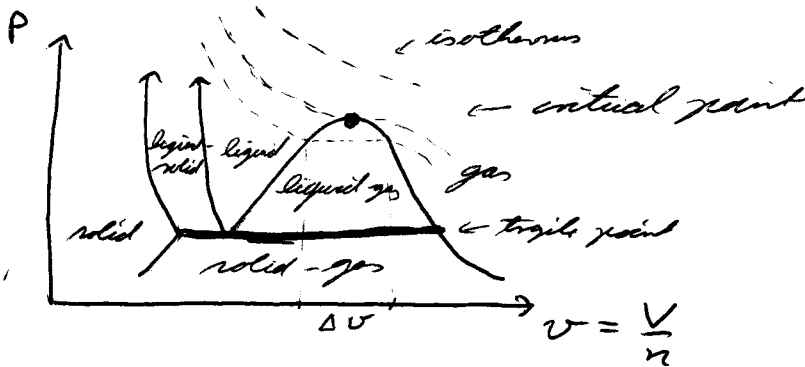
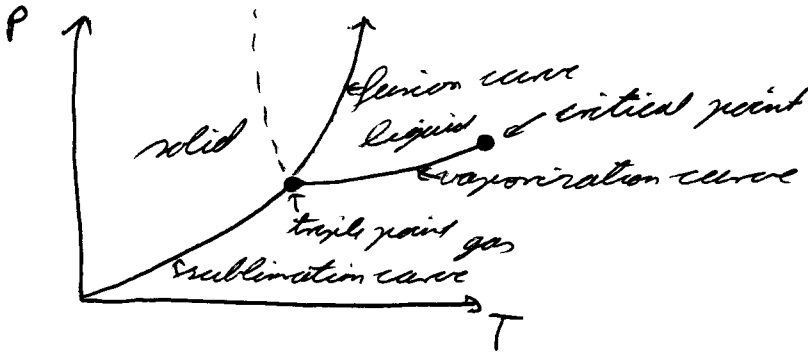
$$\Delta H = T_c \Delta S > 0$$

The latent heat of a PVT system is always positive when making a transition from a low-temperature to a high-temperature phase

II.4 Phase transition examples

II.4.1 Pure PVT systems

Typical phase diagrams



Clausius Clapeyron equation

What is the slope of coexistence lines?

know: $\mu^I(P, T) = \mu^{II}(P, T)$

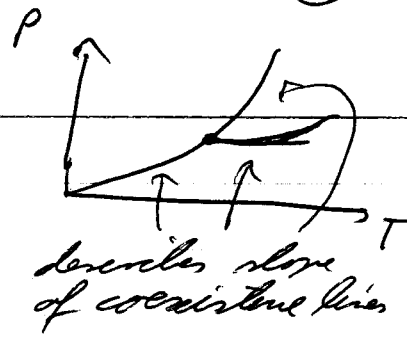
$$\Rightarrow d\mu^I = d\mu^{II}$$

$$\mu = \frac{G}{n} \Rightarrow d\mu = v dP - s dT$$

$$v = \frac{V}{n} \quad s = \frac{S}{n}$$

$$v^I dP - s^I dT = v^{II} dP - s^{II} dT$$

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}} = \frac{s^I - s^II}{v^I - v^II} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T \Delta v}$$



"Clapeyron-Clapeyron equation"

Vaporization and Sublimation curves

approximations:

- volume of fluid/solid small compared to volume of vapor
- vapor obeys ideal gas law
- latent heat Δh is constant



Δh is different for liquid-gas and solid-gas transition!

$$\Delta v \approx \frac{RT}{P}$$

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}} = \frac{P \Delta h}{RT^2}$$

$$\Rightarrow P = P_0 e^{-\frac{\Delta h}{RT}}$$

The higher the temperature the higher the vaporization/sublimation pressure.

The boiling/sublimation point is the lower the lower the pressure.

→ can measure Δh by deriving change in boiling/sublimation point

Example: NH_3 (ammonia) in vicinity of triple point:

sublimation curve measured: $\ln(P) = 27.79 - \frac{3726}{T}$

vaporization curve measured: $\ln(P) = 24.10 - \frac{3005}{T}$

(P in Pa, T in K)

What are P_t , T_t ?

$$27.79 - \frac{3726}{T_t} = 24.10 - \frac{3005}{T_t} \Rightarrow T_t = 195.4 \text{ K}$$
$$\Rightarrow P_t = 6.13 \text{ kPa}$$

What is the latent heat of sublimation?

$$(R \approx 8.3 \frac{\text{J}}{\text{mol K}})$$

$$\left(\frac{\partial P}{\partial T}\right)_{\text{curve}} = \frac{3726 P}{T^2} = \frac{P \Delta h_{\text{sg}}}{RT^2} \Rightarrow \Delta h_{\text{sg}} \approx 31 \frac{\text{kJ}}{\text{mol}}$$

What is the latent heat of vaporization?

$$\left(\frac{\partial P}{\partial T}\right)_{\text{curve}} = \frac{3005 P}{T^2} \approx \frac{P \Delta h_{\text{vg}}}{RT^2} \Rightarrow \Delta h_{\text{vg}} \approx 25 \frac{\text{kJ}}{\text{mol}}$$

warning: actually Δh depends on temperature

→ exponential law only good for relatively small temperature changes

specifically $\Delta h_{\text{vg}} \rightarrow 0$ as $T \rightarrow T_c$

↓ 10/28