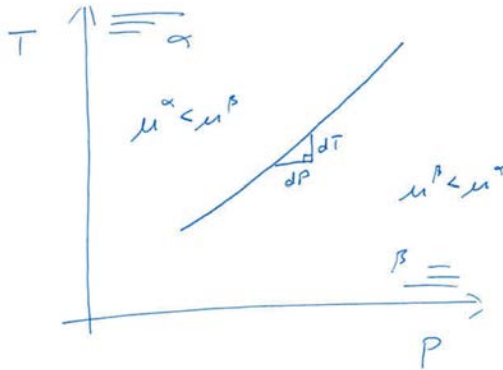


# 3.020 Lecture 11

Prof. Rafael Jaramillo

# 1 Clausius-Clapeyron equation



- On coexistence line

$$\mu^\alpha(T, P) = \mu^\beta(T, P)$$

$$d\mu^\alpha(T, P) = d\mu^\beta(T, P)$$

$$d\mu^\alpha = -S^\alpha dT + V^\alpha dP$$

$$d\mu^\beta = -S^\beta dT + V^\beta dP$$

$$d\mu^\alpha = d\mu^\beta$$

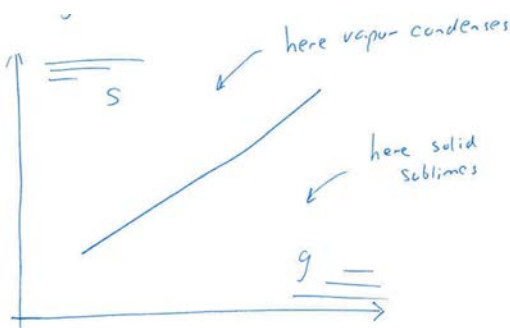
$$\Rightarrow \underbrace{(S^\alpha - S^\beta)}_{\Delta S^{\beta \rightarrow \alpha}} dT = \underbrace{(V^\alpha - V^\beta)}_{\Delta V^{\beta \rightarrow \alpha}} dP$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$$

**Clausius-Clapeyron**

for isothermal transformation  $\Delta S = \frac{\Delta H}{T}$

# 2 Using the C-C equation: Vapor pressure



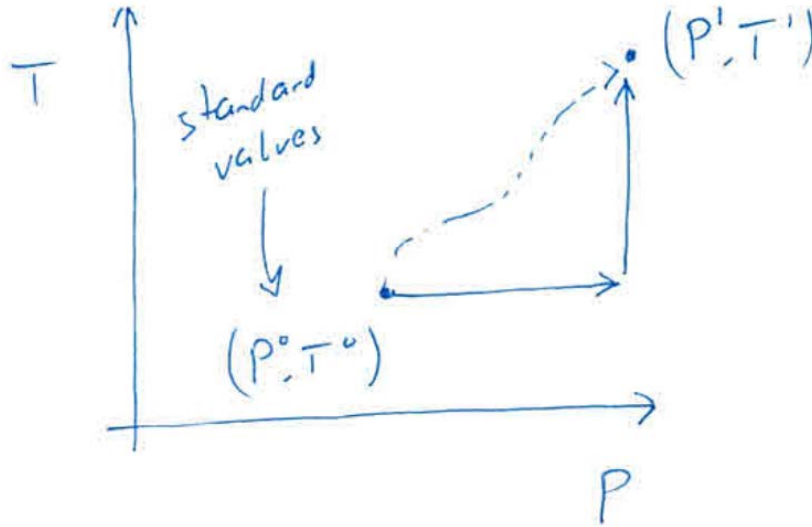
- On coexistence line, vapor pressure is saturated at  $P_{SAT}$

- If excess vapor pressure is added, vapor will condense to reapproach  $P_{SAT}$
- If vapor pressure is reduced, solid will sublime to reapproach  $P_{SAT}$
- Example of Le Chatelier principle

- Calculate  $P_{SAT}$  by integrating the CC equation

$$dP\Delta V = dT\frac{\Delta H}{T} \implies \text{need: } (\Delta H(T, P), \Delta V(T, P))$$

- Transformation quantities can be found from standard values by integrating in the  $(T, P)$  plane



- Calculating  $\Delta H(T, P)$

$$dH = C_p dT + V(1 - T\alpha)dP$$

$$\begin{aligned} \Delta H(T, P) &= \Delta H(T_0, P_0) + \int_{T_0}^T d\Delta H_P + \int_{P_0}^P d\Delta H_T \\ &= \Delta H(T_0, P_0) + \int_{T_0}^T dT' \Delta C_p + \int_{P_0}^P dP' \Delta(V(1 - T\alpha)) \end{aligned}$$

- Calculating  $\Delta V(T, P)$

$$dV = V\alpha dT - V\beta dP$$

$$\begin{aligned} \Delta V &= \Delta V(T_0, P_0) + \int_{T_0}^T d\Delta V_P + \int_{P_0}^P d\Delta V_T \\ &= \Delta V(T_0, P_0) + \int_{T_0}^T dT' \Delta(V\alpha) + \int_{P_0}^P dP' \Delta(-V\beta) \end{aligned}$$

- In general this requires knowing  $C_P(T, P), V'(T, P), \alpha(T, P), \beta(T, P)$  for both phases
  - For vaporization of a condensed phase over a limited temp. range, can simplify using 3 assumptions :
    1.  $\Delta H \approx \text{const.}$
    2.  $V^g \gg V^s, V^l \implies |\Delta V| \approx V^g$
    3. Gas behaves ideally
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### 3 Gibbs phase rule: how many phases can coexist at equilibrium ?

# deg of freedom = # variables - # independent constraints

Handwritten diagram illustrating the derivation of the Gibbs phase rule:

- A list of variables for  $Ph$  phases:  $(T, P)^a, (T, P)^b, \dots$ . A bracket groups these as " $Ph$  phases".
- Below this list, a bracket groups the variables as " $2 \text{ vars.}$ ".
- An arrow points to the equation:  $\implies \# \text{ vars} = 2 * Ph$ .

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DoF =  $2 Ph - 3 (Ph - 1) = 3 - Ph$ , **Gibbs phase rule for nary systems**

- 1 phase region  $\rightarrow$  DoF = 2, e.g. (T,P) plane
- 2 phase region  $\rightarrow$  DoF = 1, e.g. coexistence line
- 3 phase region  $\rightarrow$  DoF = 0, e.g. triple point

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