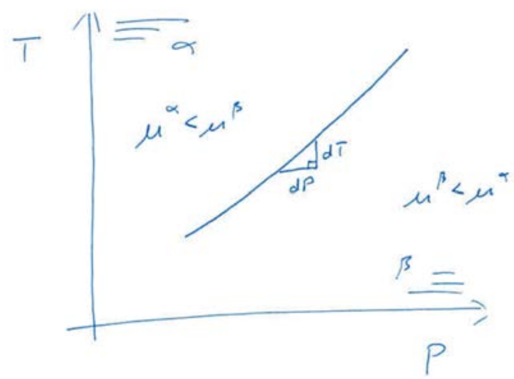
3.020 Lecture 11

Prof. Rafael Jaramillo

1 Clausius-Clapeyron equation



- On coexistence line

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

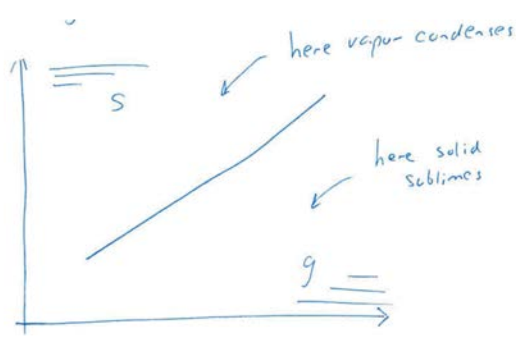
$$\begin{aligned} d\mu^\alpha &= -S^\alpha dT + V^\alpha dP \\ d\mu^\beta &= -S^\beta dT + V^\beta dP \\ d\mu^\alpha &= d\mu^\beta \\ \implies \quad (\underbrace{S^\alpha - S^\beta}_{\Delta S^{\beta\to\alpha}})dT &= (\underbrace{V^\alpha - V^\beta}_{\Delta V^{\beta\to\alpha}})dP \end{aligned}$$

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

Clausius-Clapeyron

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

2 Using the C-C equation: Vapor pressure

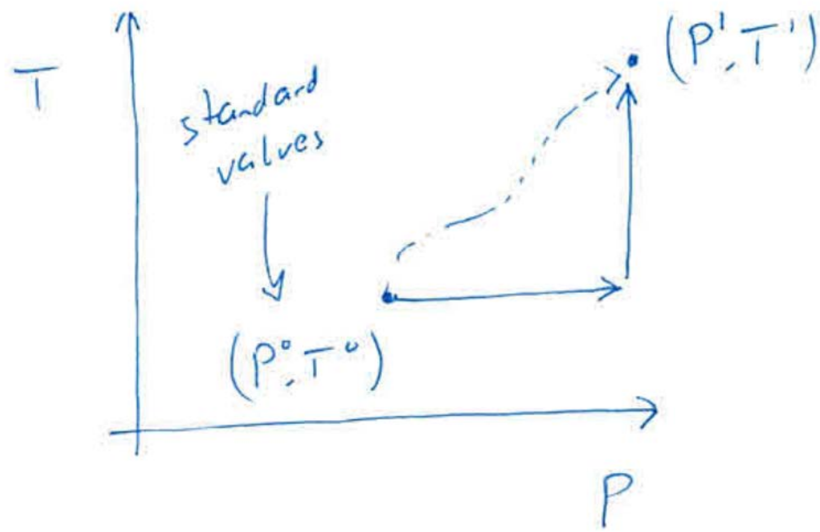


- On coexistence line, vapor pressure is <u>saturated</u> at P_{SAT}
  - If excess vapor pressure is added, vapor will condense to reapproach P_{SAT}
  - If vapor pressure is reduced, solid will sublime to reapproach P_{SAT}
  - Example of Le Chatelier principle

- Calculate P_{SAT} by integrating the CC equation

$$dP\Delta V = dT\frac{\Delta H}{T} \quad \Longrightarrow \quad \textbf{need:} \quad (\Delta H(T,P), \Delta V(T,P))$$

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



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

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

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

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

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

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

- 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. $\Delta H \approx$ const.
    2. $V^g \gg V^S, V^l \implies |\Delta V| \approx V^g$
    3. Gas behaves ideally

---

3 Gibbs phase rule: how many phases can coexist at equilibrium ?

\# deg of freedom = \# variables - \# independent constraints

\# vars

$$\left.\underbrace{\begin{array}{l}(T,P)^\alpha\\(T,P)^\beta\\ \vdots\end{array}}_{2\text{ vars.}}\right\}\text{Ph phases} \implies \#\text{ vars} = 2 * \text{Ph}$$

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

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