3.020 Lecture 11

Prof. Rafael Jaramillo
1 Clausius-Clapeyron equation

\[ \mu^\alpha(T, P) = \mu^\beta(T, P) \]

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

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

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

\[ dP\Delta V = dT \frac{\Delta H}{T} \implies \textbf{need: } (\Delta H(T, P), \Delta V(T, P)) \]

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

\[
\begin{align*}
\Delta H(T, P) &= \Delta H(T_0, P_0) + \int_{T_0}^{T} dT' \Delta C_p + \int_{P_0}^{P} dP' \Delta (V(1 - T\alpha)) \\
\Delta V(T, P) &= \Delta V(T_0, P_0) + \int_{T_0}^{T} dT' \Delta (V\alpha) + \int_{P_0}^{P} dP' \Delta (-V\beta)
\end{align*}
\]
• 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

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

# deg of freedom = # variables - # independent constraints

\[
\begin{array}{c}
\text{# vars} \\
\{ (T, P) \} \\
\vdots
\end{array} \quad \Rightarrow \quad \text{# vars} = 2 \times \text{Ph}
\]

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