



P-V diagram displays single and two phase coexistence region, a critical point, and a triple line.

$$T_1 < T_2 < T_3 < T_4$$

P-V-T diagram for ideal gas in section.

8.5 - Providing a theoretical basis for the P-T Phase diagram

$$\mu_{\alpha}(P,T) = \mu_{\beta}(P,T)$$

$$P, T \rightarrow P \propto dP$$

$$\mu_{\alpha}(P,T) + d\mu_{\alpha} = \mu_{\beta}(P,T) + d\mu_{\beta}$$

↳ for two phases to remain in equilibrium

$$d\mu_{\alpha} = d\mu_{\beta}$$

Because $d\mu$ can be expressed in terms of dT and dP

$$d\mu_{\alpha} = -S_{m\alpha}dT + V_{m\alpha}dP \quad d\mu_{\beta} = -S_{m\beta}dT + V_{m\beta}dP$$

$d\mu$ can be equated & integ

$$(S_{m\beta} - S_{m\alpha})dT = (V_{m\beta} - V_{m\alpha})dP \quad \text{or}$$

$$-S_{m\alpha}dT + V_{m\alpha}dP = -S_{m\beta}dT + V_{m\beta}dP$$

Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{S_{m\beta} - S_{m\alpha}}{V_{m\beta} - V_{m\alpha}}$$

$$\Delta G_{\text{fusion}} = \Delta H_{\text{fusion}} - T\Delta S_{\text{fusion}} = 0$$

$$\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} \approx \frac{22 \text{ J/mol K}}{\pm 4.0 \times 10^{-6} \text{ m}^3/\text{mol}}$$

$$= \pm 5.5 \times 10^6 \text{ Pa K}^{-1} = \pm 5.5 \text{ bar K}^{-1}$$

$$\left(\frac{dP}{dT}\right)_{\text{vaporization}} = \frac{\Delta S_{\text{vaporization}}}{\Delta V_{\text{vaporization}}} \approx \frac{95 \text{ J mol}^{-1} \text{ K}^{-1}}{2 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}} = 4.8 \times 10^3 \text{ Pa K}^{-1}$$

8.6 - Using Clausius - Clapeyron equation to Calculate vapor pressure as a function of T

$$\int_{P_i}^{P_f} df = \int_{T_i}^{T_f} \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} dT = \int_{T_i}^{T_f} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{dT}{T} \approx \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \int_{T_i}^{T_f} \frac{dT}{T}$$

$$P_f - P_i = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{T_f}{T_i} = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\ln T_i + \Delta T}{T_i} \approx \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{\Delta T}{T_i}$$

Clausius-Claperson Equation:

$$\frac{dp}{dT} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \approx \frac{\Delta H_{\text{vap}}}{\Delta V_{\text{vap}}} = \frac{P \Delta H_{\text{vap}}}{RT^2} \quad \int_{P_i}^{P_f} \frac{dp}{P} = \frac{\Delta H_{\text{vap}}}{R} \int_{T_i}^{T_f} \frac{dT}{T^2}$$

$$\frac{dp}{P} = \frac{\Delta H_{\text{vap}}}{R} \frac{dT}{T^2}$$

$$\ln \frac{P_f}{P_i} = - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

8.7 - The vapor pressure of a pure substance depends on the applied pressure

$$m_{\text{liquid}}(T, P) = m_{\text{gas}}(T, P)$$

$$\left(\frac{dm_{\text{liquid}}(T, P)}{dP} \right)_T = \left(\frac{dm_{\text{gas}}(T, P)}{dP} \right)_T \left(\frac{dP}{dP} \right)_T$$

$$V_m = V_m^{\text{gas}} \left(\frac{dP}{dP} \right)_T \quad \text{or} \quad \left(\frac{dP}{dP} \right)_T = \frac{V_m^{\text{liquid}}}{V_m^{\text{gas}}}$$

$$\frac{RT}{P} dP = V_m^{\text{liquid}} dP \quad \text{or} \quad RT \int_{P^*}^P \frac{dP'}{P'} = V_m^{\text{liquid}} \int_{P^*}^P dP'$$

Integrate

$$RT \ln \left(\frac{P}{P^*} \right) = V_m^{\text{liquid}} (P - P^*)$$

$$\ln \left(\frac{P}{P^*} \right) = \frac{V_m^{\text{liq}} (P - P^*)}{RT}$$