8.5 Providing a Theoretical Basis for the P–T Phase Diagram

- the clapeyron equation is developed which allows us to calculate the slope of the coexistence curves in a P–T phase diagram if ΔS_m and ΔV_m for the transition are known

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

- we also get Trouton's rule, which states that $\Delta S_{vaporization} \approx 90\ J\ mol^{-1} K^{-1}$ for liquids.
- slope of liquid-gas coexistence curve given by

$$\left(\frac{dP}{dT}\right)_{vaporization} = \frac{\Delta S_{vaporization}}{\Delta V_{vaporization}} = \frac{95\ J\ mol^{-1} K^{-1}}{2.0 \times 10^{-2} m^3 mol^{-1}} \approx 4.8 \times 10^3\ Pa\ K^{-1}$$
$$= 4.8 \times 10^{-2}\ bar\ K^{-1}$$

8.6 Using the Clausius-Clapeyron Equation to Calculate Vapor Pressure as a Function of T

- clausius-clapeyron equation - obtained assuming ideal gas law holds for a liquid-gas coexistence curve, we have $\Delta V \approx \Delta V^{gas}$

$$\frac{dP}{dT} = \frac{\Delta S_{vaporization}}{\Delta V_{vaporization}} \approx \frac{\Delta H_{vaporization}}{T V_m^{gas}} = \frac{P \Delta H_{vaporization}}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_{vaporization}}{R} \frac{dT}{T^2}$$

- $$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_{vaporization}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$$

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