

CHEM 3410: Physical Chemistry I — Fall 2009

October 19, 2009

Lecture 20: The Clapeyron Equation

References

1. Levine, *Physical Chemistry*, Sections 7.1–7.4

Key Concepts

- At equilibrium, the free energy is minimized. Therefore, the phase with the lowest chemical potential will be stable.
- To understand the shape of the phase boundaries in single component systems, we derived the Clapeyron equation. This was possible because along the phase boundary, the chemical potential of both phases are equal. If we have a boundary between an α phase and β phase:

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}} = \frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta\bar{V}_{\alpha\rightarrow\beta}}$$

where $\Delta\bar{S}_{\alpha\rightarrow\beta}$ and $\Delta\bar{V}_{\alpha\rightarrow\beta}$ are the change in molar entropy and volume, respectively, in going from the α to β phase.

- Since for a single component system, $\mu = \bar{G} = \bar{H} - T\bar{S}$, the Clapeyron equation can be rewritten in terms of the enthalpy of the transformation:

$$\left(\frac{dP}{dT}\right)_{\text{coexistence}} = \frac{\Delta\bar{H}_{\alpha\rightarrow\beta}}{T\Delta\bar{V}_{\alpha\rightarrow\beta}}$$

- For a simple diagram with only solid, liquid, and gas phases we can determine the relative slopes of the boundaries by considering the differences in molar entropy and volume for each transition. For example, we would expect the liquid to gas boundary to have a small positive slope while the transition from the solid to gas would have a larger (steeper) positive slope.
- The slope of the solid-liquid boundary depends on difference in molar volume of the solid and liquid phases. For water, the liquid phase has a higher density (smaller molar volume) meaning the boundary on the phase diagram will have large negative slope. Most other substances have a large positive slope because the solid is denser than the liquid.
- For a condensed phase (solid or liquid) in equilibrium with a gas we derived the Clausius-Clapeyron equation by treating the gas as ideal and assuming the molar volume of the gas is much larger than that of the condensed phase. For liquid-vapor equilibrium:

$$d \ln P = \frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{RT^2} dT$$

For solid-vapor equilibrium, the ΔH_{vap} would be replaced by $\Delta H_{\text{sublimation}}$.

- If the enthalpy is independent of temperature over our temperature range of interest then we can relate the vapor pressure of the gas at one temperature and pressure (T_1, P_1) to the vapor pressure at another temperature (T_2, P_2) .

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{trans}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where ΔH_{trans} is either the enthalpy of sublimation or vaporization, depending on the phases involved.

Related Exercises in Levine

Exercises: 7.22, 7.24