12.8: The Clapeyron Equation

The analysis in the two previous sections can be repeated for any phase change of a pure substance. Let α and β denote the two phases that are at equilibrium.

$$\alpha \rightleftharpoons \beta$$

Let $\overline{G}_\alpha$, $\overline{S}_\alpha$, and $\overline{V}_\alpha$ represent the Gibbs free energy, the entropy, and the volume of one mole of pure phase α at pressure P and temperature T. Let $\overline{G}_\beta$, $\overline{S}_\beta$, and $\overline{V}_\beta$ represent the corresponding properties of one mole of pure phase β. The equations

$$d\overline{G}\left(\alpha\right)=\overline{V}_\alpha dP-\overline{S}_\alpha dT$$

and

$$d\overline{G}\left(\beta\right)=\overline{V}_\beta dP-\overline{S}_\beta dT$$

describe the changes in the Gibbs free energy of a mole of α and a mole of β when they go from one $\alpha-\beta$-equilibrium state at P and T to a second $\alpha-\beta$-equilibrium state at $P+dP$ and $T+dT$. Since these Gibbs free energy changes must be equal, we have

$$\begin{aligned} d\overline{G}\left(\beta\right)-d\overline{G}\left(\alpha\right) &=\left(\overline{V}_\beta-\overline{V}_\alpha\right)dP-\left(\overline{S}_\beta-\overline{S}_\alpha\right)dT \\ &=\Delta\overline{V}\,dP-\Delta\overline{S}dT \\ &=0 \end{aligned}$$

and

$$\frac{dP}{dT}=\frac{\Delta\overline{S}}{\Delta\overline{V}}$$

where $\Delta\overline{S}$ and $\Delta\overline{V}$ are the entropy and volume changes that occur when one mole of the substance goes from phase α to phase β. Since $\Delta\overline{S}=\Delta\overline{H}/T$, the condition for equilibrium between phases α and β becomes

$$\frac{dP}{dT}=\frac{\Delta\overline{H}}{T\,\Delta\overline{V}} \tag{12.8.1}$$

Equation 12.8.1 is known as the **Clapeyron equation**.