

12.9: The Clausius-Clapeyron Equation

To use the Clapeyron equation we must know the enthalpy and volume differences at one equilibrium temperature and pressure. In general, these properties are readily measured. If we fix the pressure, we can measure the corresponding equilibrium temperature. We can obtain the enthalpy change at this pressure by measuring the heat required to convert a mole of the substance from one phase to the other. We can obtain the volume change from the molar volumes, which we can obtain by measuring the density of each phase. The enthalpy of the phase change varies only weakly as the equilibrium pressure and temperature vary. Similarly, for condensed phases, the densities are weak functions of temperature. This means that, for transitions between condensed phases, $\Delta\bar{H}/\Delta\bar{V}$ is approximately constant over a modest temperature range.

For a sublimation or vaporization process, the product is a gas. Then the molar volume of the product is a sensitive function of both pressure and temperature. However, the molar volume of the product phase is much greater than the molar volume of the initial solid or liquid phase. To a good approximation, the volume change for the process equals the volume of the gas produced. If we have an equation of state for the gas, the volume calculated from the equation of state is a good approximation to $\Delta\bar{V}$ for the phase change. The ideal gas equation is usually adequate for this purpose. Then, $\Delta\bar{V} \approx RT/P$, and

$$\frac{dP}{dT} = \frac{P\Delta\bar{H}}{RT^2} \quad (\text{Clausius-Clapeyron equation})$$

This equation for the pressure–temperature relationship for a phase equilibrium involving a gas is called the **Clausius-Clapeyron equation**. Dividing both sides by the pressure, we can put the Clausius-Clapeyron equation into an alternative and often-useful form:

$$\frac{d\ln P}{dT} = \frac{\Delta\bar{H}}{RT^2}$$

If we can assume that $\Delta\bar{H}$ is independent of pressure, we can separate variables and integrate to obtain the Clausius-Clapeyron equation in integrated form. If we can assume further that $\Delta\bar{H}$ is constant, the integration yields

$$\int_{P_0}^P \frac{dP}{P} = \frac{\Delta\bar{H}}{R} \int_{T_0}^T \frac{dT}{T^2}$$

and

$$\ln \frac{P}{P_0} = -\frac{\Delta\bar{H}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

where P_0 and T_0 are the initial equilibrium position.

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