

## 12.4: The Clausius-Clapeyron Equation

Let's now take a closer look at the equilibrium between a condensed phase and the gas phase. For both the vaporization and sublimation processes, Clausius showed that the Clapeyron equation can be simplified by using:

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T} \quad \Delta\bar{V} = \bar{V}_{\text{g}} - \bar{V}_{\text{l}} \cong \bar{V}_{\text{g}}, \quad (12.4.1)$$

resulting in:

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}}S}{\Delta\bar{V}} \cong \frac{\Delta_{\text{vap}}H}{T\bar{V}_{\text{g}}}. \quad (12.4.2)$$

Using the ideal gas law to replace the molar volume of the gas, we obtain:

$$\frac{dP}{dT} = \frac{P\Delta_{\text{vap}}H}{RT^2}, \quad (12.4.3)$$

which can be rearranged as:

$$\frac{dP}{P} = \frac{\Delta_{\text{vap}}H}{R} \frac{dT}{T^2}. \quad (12.4.4)$$

Equation 12.4.4 is known as the **Clausius–Clapeyron equation**, and it measures the dependence of the vapor pressure of a substance as a function of the temperature. The Clausius–Clapeyron equation can be integrated to obtain:

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta_{\text{vap}}H}{R} \int_{T_i}^{T_f} \frac{dT}{T^2} \\ \ln \frac{P_f}{P_i} = -\frac{\Delta_{\text{vap}}H}{R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right).$$

The integrated Clausius–Clapeyron equation shows that the vapor pressure depends exponentially on the temperature. Thus, even a small change in the temperature will result in a significant change in the vapor pressure. In fact, we daily use the fact that the vapor pressure of water changes drastically when we increase its temperature for cooking most of our food. For example, at an external pressure of 1 bar, it rapidly grows from  $P^* = 0.02$  bar to  $P^* = 1$  bar when the temperature is increased from  $T = 293$  K (around room temperature) to  $T = 373$  K (boiling point). The integrated Clausius–Clapeyron equation is also often used to determine the enthalpy of vaporization from measurements of vapor pressure at different temperatures.

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