

7.2: Partial Pressure Measurements and Raoult's Law

It is fantastic that we have a simple way to quantify the changes in the thermodynamic variables of liquids by hijacking measurements of the equilibrated vapor phase's μ , as determined by the change in the vapor's partial pressure. And thus we can mix any two miscible substances, salt and water or perhaps something more risqué like gin and juice (ethanol and water) and measure the changes in the individual substances' vapor pressures to determine ΔG_m , ΔH_m , and ΔS_m for mixing. However, the measurement of partial pressure of a vapor is rather complex even by today's standards. Perhaps there is an easier way to relate the partial pressure of a vapor to the concentration of the liquid in solution? For example, if we have a cup of pure water then the partial pressure of the H_2O vapor is 3,200 Pa. Upon dilution with an extremely large quantity of ethanol the water partial pressure must drop to almost nothing, ~ 0 Pa. Thus, the water vapor's partial pressure decreases from 3,200 Pa \rightarrow 0 Pa as χ_{H_2O} decreases from 1 \rightarrow 0, where χ_{H_2O} is water's mole fraction in the liquid solution.

François-Marie Raoult, an electrochemist, discovered that a vapor's partial pressure may be linear function of the liquid's molar concentration, especially if the liquid is very dilute. Mathematically this is expressed as:

$$P_i = P_i^* \cdot \frac{n_i}{n_{total}} = P_i^* \cdot \chi_i \quad (7.2.1)$$

Equation 7.2.1 is Raoult's Law, and note how it yields the pure partial pressure if the i^{th} species is pure ($\chi_i = 1$) and 0 Pa if the i^{th} species is infinitely diluted ($\chi_i = 0$). Shown in Figure 7.2 A is a graph of the partial pressures of benzene + toluene solution as a function of their mole fractions, including lines derived from equation 7.2. The use of Raoult's Law is ideal as it provides a near-perfect fit over the entire concentration range! However, shown in Figure 7.2 B are data for a water + ethanol solution, which demonstrates that Raoult's Law doesn't always work well. These situations are less than ideal and will be discussed further in later sections of this chapter.

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