

## 6.13: Phase Diagrams of Non-Ideal Solutions

Non-ideal solutions follow [Raoult's law](#) for only a small amount of concentrations. The typical behavior of a non-ideal solution with a single volatile component is reported in the  $Px_B$  plot in Figure 6.13.1.

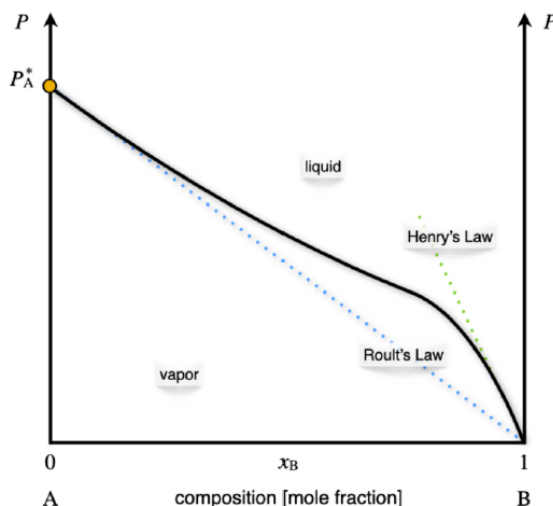


Figure 6.13.1: The Pressure–Composition Phase Diagram of a Non-Ideal Solution Containing a Single Volatile Component at Constant Temperature.

Raoult's behavior is observed for high concentrations of the volatile component. This behavior is observed at  $x_B \rightarrow 0$  in Figure 6.13.1, since the volatile component in this diagram is A. At low concentrations of the volatile component  $x_B \rightarrow 1$  in Figure 6.13.1, the solution follows a behavior along a steeper line, which is known as **Henry's law**. William Henry (1774–1836) has extensively studied the behavior of gases dissolved in liquids. His studies resulted in a simple law that relates the vapor pressure of a solution to a constant, called Henry's law solubility constants:

$$P_B = k_{AB}x_B, \quad (6.13.1)$$

where  $k_{AB}$  depends on the chemical nature of A and B. The corresponding diagram for non-ideal solutions with two volatile components is reported on the left panel of Figure 6.13.2. The total pressure is once again calculated as the sum of the two partial pressures. Positive deviations on Raoult's ideal behavior are not the only possible deviation from ideality, and negative deviation also exists, albeit slightly less common. An example of a negative deviation is reported in the right panel of Figure 6.13.2

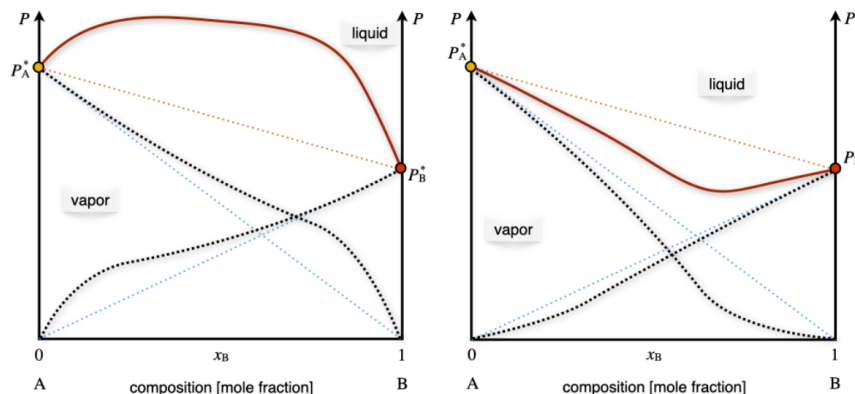


Figure 6.13.2: The Pressure–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Temperature.

If we move from the  $Px_B$  diagram to the  $Tx_B$  diagram, the behaviors observed in Figure 6.13.2 will correspond to the diagram in Figure 6.13.3

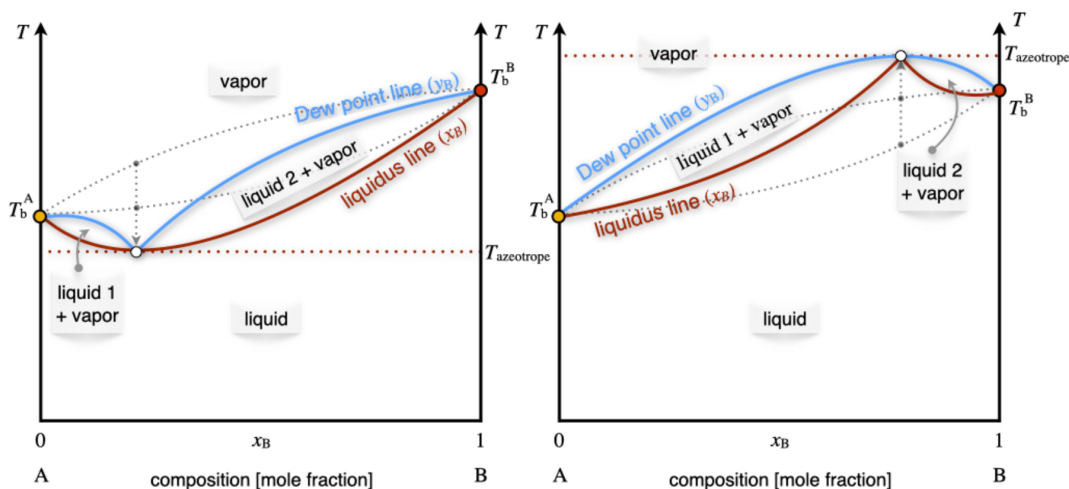


Figure 6.13.3: The Temperature–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Pressure.

The minimum (left plot) and maximum (right plot) points in Figure 6.13.3 represent the so-called **azeotrope**.

An azeotrope is a constant boiling point solution whose composition cannot be altered or changed by simple distillation. This happens because the liquidus and Dew point lines coincide at this point. Therefore, the liquid and the vapor phases have the same composition, and distillation cannot occur. Two types of azeotropes exist, representative of the two types of non-ideal behavior of solutions. The first type is the positive azeotrope (left plot in Figure 6.13.3). A notorious example of this behavior at atmospheric pressure is the ethanol/water mixture, with composition 95.63% ethanol by mass. This positive azeotrope boils at  $T = 78.2\text{ }^{\circ}\text{C}$ , a temperature that is lower than the boiling points of the pure constituents, since ethanol boils at  $T = 78.4\text{ }^{\circ}\text{C}$  and water at  $T = 100\text{ }^{\circ}\text{C}$ . The second type is the negative azeotrope (right plot in Figure 6.13.3). An example of this behavior at atmospheric pressure is the hydrochloric acid/water mixture with composition 20.2% hydrochloric acid by mass. This negative azeotrope boils at  $T = 110\text{ }^{\circ}\text{C}$ , a temperature that is higher than the boiling points of the pure constituents, since hydrochloric acid boils at  $T = -84\text{ }^{\circ}\text{C}$  and water at  $T = 100\text{ }^{\circ}\text{C}$ .

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