

8.8: Non-ideality - Henry's Law and Azeotropes

The preceding discussion was based on the behaviors of ideal solutions of volatile compounds, and for which both compounds follow Raoult's Law. **Henry's Law** can be used to describe these deviations.

$$p_B = k_H p_B^{\circ}$$

For which the Henry's Law constant (k_H) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in Figure 8.8.1.

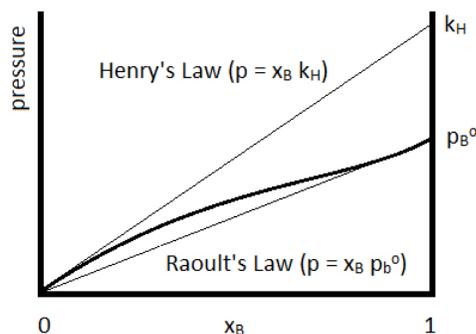


Figure 8.8.1: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

✓ Example 8.8.1: Solubility of Carbon Dioxide in Water

The solubility of $CO_2(g)$ in water at 25 °C is $3.32 \times 10^{-2} \text{ M}$ with a partial pressure of CO_2 over the solution of 1 bar. Assuming the density of a saturated solution to be 1 kg/L, calculate the Henry's Law constant for CO_2 .

Solution

In one L of solution, there is 1000 g of water (assuming the mass of CO_2 dissolved is negligible.)

$$(1000 \text{ g}) \left(\frac{1 \text{ mol}}{18.02 \text{ g}} \right) = 55 \text{ mol } H_2O$$

The solubility of CO_2 can be used to find the number of moles of CO_2 dissolved in 1 L of solution also:

$$\frac{3.32 \times 10^{-2} \text{ mol}}{L} \cdot 1 \text{ L} = 3.32 \times 10^{-2} \text{ mol } CO_2$$

and so the mol fraction of CO_2 is

$$\chi_b = \frac{3.32 \times 10^{-2} \text{ mol}}{55.5 \text{ mol}} = 5.98 \times 10^{-4}$$

And so

$$10^5 \text{ Pa} = 5.98 \times 10^{-4} k_H$$

or

$$k_H = 1.67 \times 10^9 \text{ Pa}$$

Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

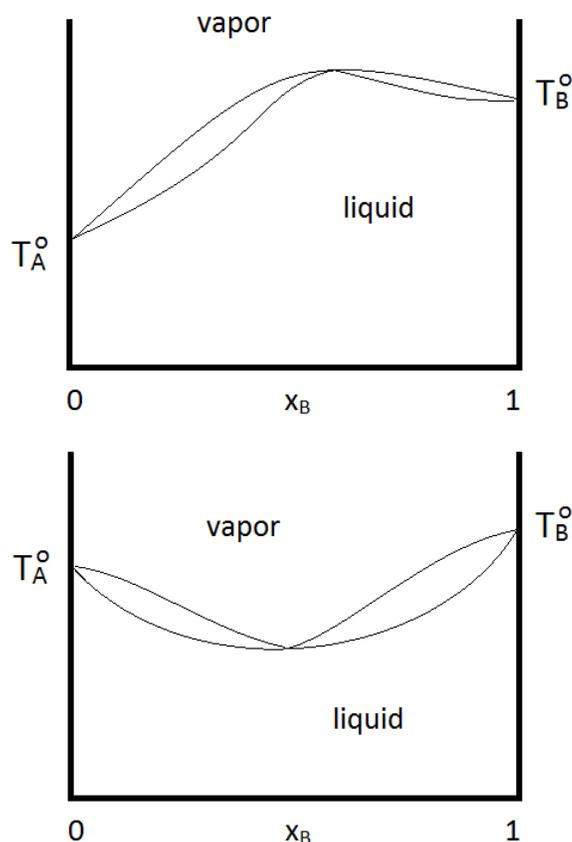


Figure 8.8.2: Phase diagrams for (left) a maximum boiling point azeotrope and (right) a minimum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as shown in Figure 8.8.2; *left*. Regardless, distillation cannot purify past the azeotrope point, since the vapor and liquid phases have the same composition. If a system forms a minimum boiling azeotrope and also has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure 8.8.3; *right*.

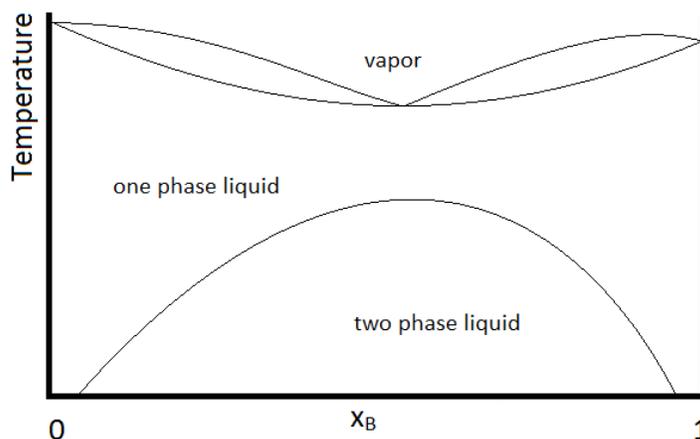
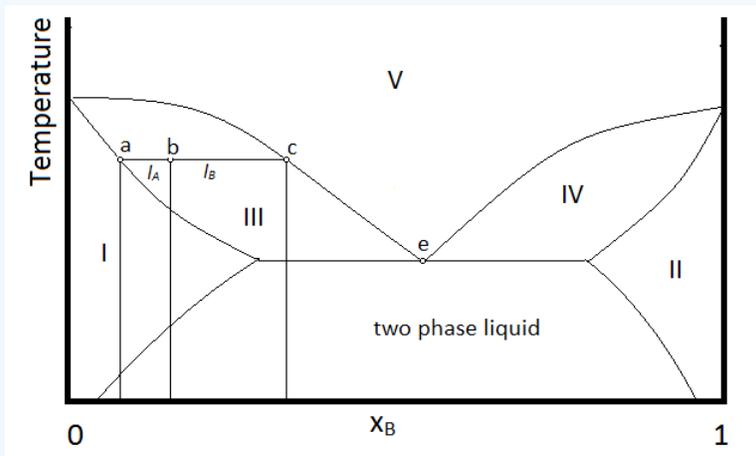


Figure 8.8.3: Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher than when components are miscible (single phase).

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look like Figure 8.8.3.

✓ Example 8.8.1:

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.



- I. Single phase liquid (mostly compound A)
- II. Single phase liquid (mostly compound B)
- III. Single phase liquid (mostly A) and vapor
- IV. Single phase liquid (mostly B) and vapor
- V. Vapor (miscible at all mole fractions since it is a gas)

Solution

Within each two-phase region (III, IV, and the two-phase liquid region), the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines l_A and l_B .

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