Video 10.7

Azeotropes and Immiscible Phases
At 90 °C (between the two pure component boiling points) the composition of the liquid is 59 mol% 1-propanol (point a) and the vapor is 45 mol% 1-propanol (point b).

*Fractional distillation: vapor is condensed and revaporized many times a to b to c to d to ... and finally you get to the pure lower boiling component at the top (the coolest point) of a distillation head!*

(from Video 10.5)
Fractional Distillation (Non-Ideal)

Fractional distillation: vapor is condensed and revaporized many times a to b to c to d to e to f, but, irrespective of initial composition, ultimately an azeotropic composition is reached (about 55:45 above) that cannot be further separated by distillation!

Using Dalton’s/Raoult’s laws:

\[ y_2 = \frac{P_2}{760 \text{ torr}} \lim_{x_2 \to 1} 760 \text{ torr} = \frac{x_2 P^*_2}{760 \text{ torr}} \]

and Dalton’s/Henry’s laws:

\[ y_2 = \frac{P_2}{760 \text{ torr}} \lim_{x_2 \to 0} 760 \text{ torr} = \frac{x_2 k_{H,2}}{760 \text{ torr}} \]

bp as a function of composition

Deviation from ideality permits the vapor phase to be enriched in either component depending on liquid composition.

Distillation of benzene-rich mixture

Distillation of ethanol-rich mixture

Fractional distillation: vapor is condensed and revaporized many times a to b to c to d to e to f, but, irrespective of initial composition, ultimately an azeotropic composition is reached (about 55:45 above) that cannot be further separated by distillation!
Self-assessment

What purification \textit{can} be accomplished for a liquid mixture that is not already at the azeotropic composition?
If not already at the azeotropic composition, the azeotrope at the top of the distillation head will be carrying away a *greater* fraction of one component than is present in the liquid. The remaining liquid will necessarily then *decrease* in that component until it is completely depleted, leaving the pure liquid of the *other* component behind.

Thus, starting from *a*, we could boil off azeotrope to leave pure EtOH, while starting from *a*, we could boil off azeotrope to leave pure benzene. However, we would not be able to use distillation to further purify the azeotropic fractions that we collected — some other method would need to be found.
Limit of Non-ideality: Immiscibility

Consider a mixture in which positive deviations from ideal behavior become larger and larger as the temperature is lowered. In the figure to the left $T_3 > T_c > T_2 > T_1$ (also note that the pressure is normalized by the vapor pressure of the pure component 2). At $T_3$ (i.e., high temp), the slope is positive everywhere. But, at $T_c$ the curve has an inflection point where:

$$\left( \frac{\partial P_2}{\partial x_2} \right) = 0$$
$$\left( \frac{\partial^2 P_2}{\partial x_2^2} \right) = 0$$

Below $T_c$ the two liquids are not miscible and they phase separate to form two separate phases. E.g., at $T_2$ one phase forms with composition $x_2'$ and another phase forms with composition $x_2''$. As the temperature is decreased the two phases become increasingly pure.
Temperature Composition Diagrams

The “critical” or “consulate” temperature

Lever rule:

\[
\frac{n'}{n''} = \frac{n'_1 + n'_2}{n''_1 + n''_2} = \frac{x''_2 - x_2}{x_2 - x'_2}
\]
\[ dU = \delta q + \delta w \]

Next: Regular Solutions