Statistical Molecular Thermodynamics

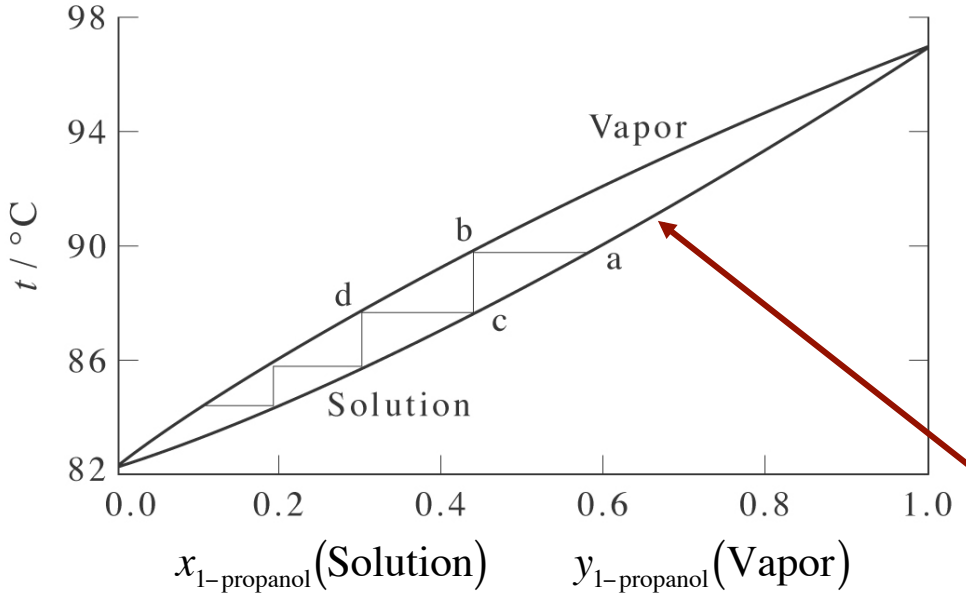
Christopher J. Cramer

Video 10.7

Azeotropes and Immiscible Phases

Fractional Distillation (Ideal)

1-propanol/2-propanol at 760 torr



(from Video 10.5)

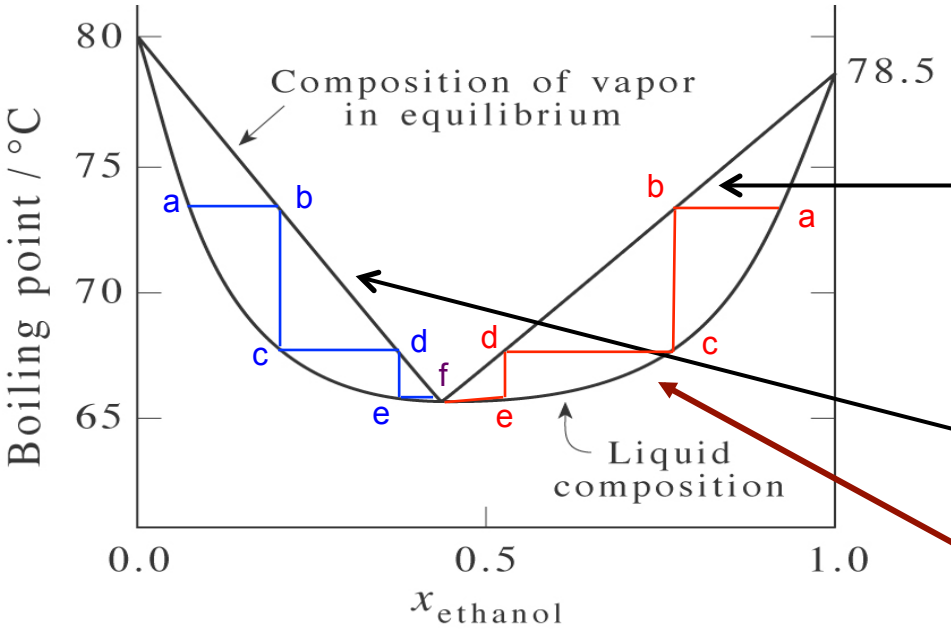
bp as a function of composition

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!

Fractional Distillation (Non-Ideal)

benzene/ethanol at 760 torr



Using Dalton's/Raoult's laws:

$$y_2 = \frac{P_2}{760\ \text{torr}} \underset{\lim x_2 \to 1}{=} \frac{x_2 P_2^*}{760\ \text{torr}}$$

and Dalton's/Henry's laws:

$$y_2 = \frac{P_2}{760\ \text{torr}} \underset{\lim x_2 \to 0}{=} \frac{x_2 k_{\text{H},2}}{760\ \text{torr}}$$

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

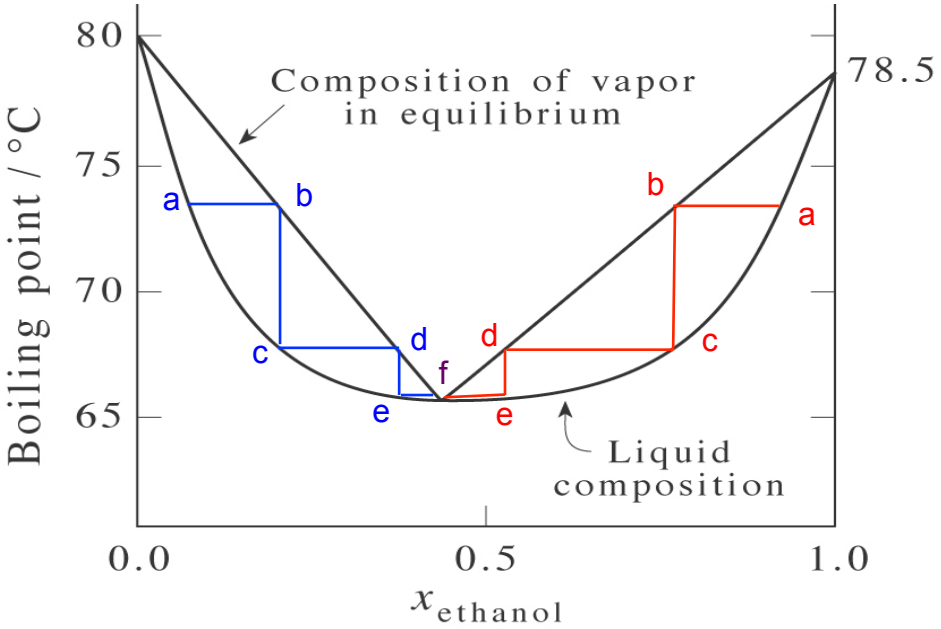
Distillation of ethanol-rich mixture

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 *can* be accomplished for a liquid mixture that is not already at the azeotropic composition?

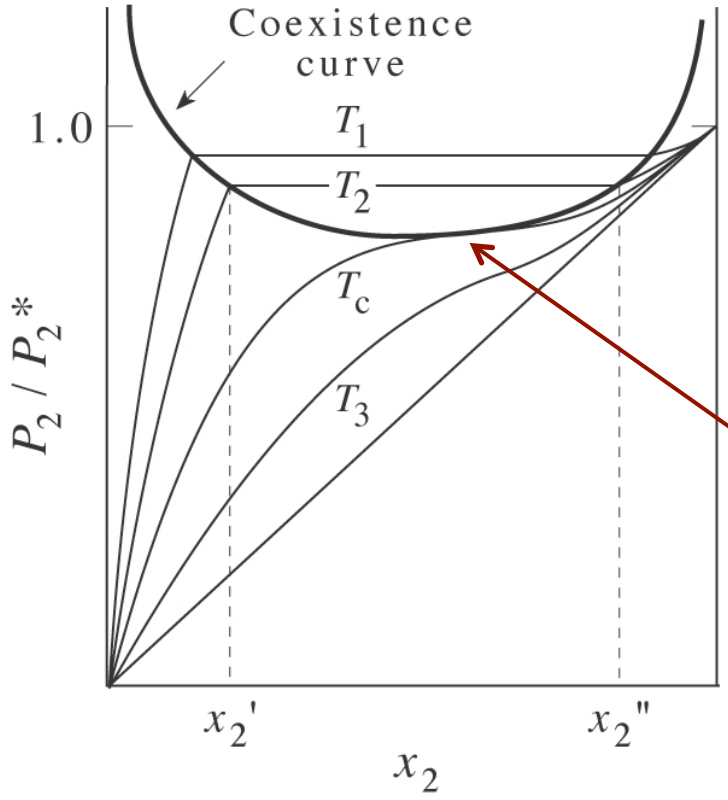
Self-assessment Explained



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



Relevant to fractional crystallization

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:

Inflection point

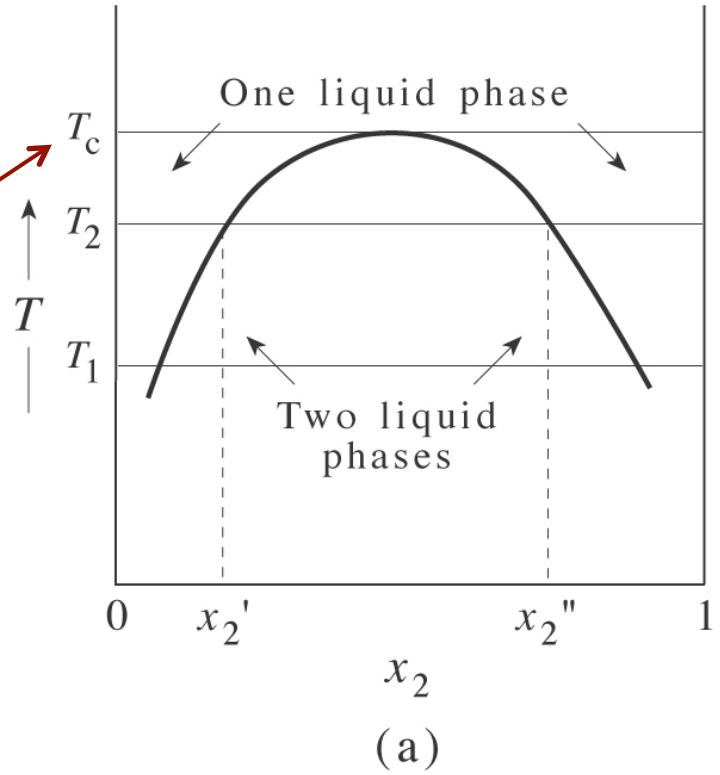
$$\left(\frac{\partial P_2}{\partial x_2}\right) = 0$$

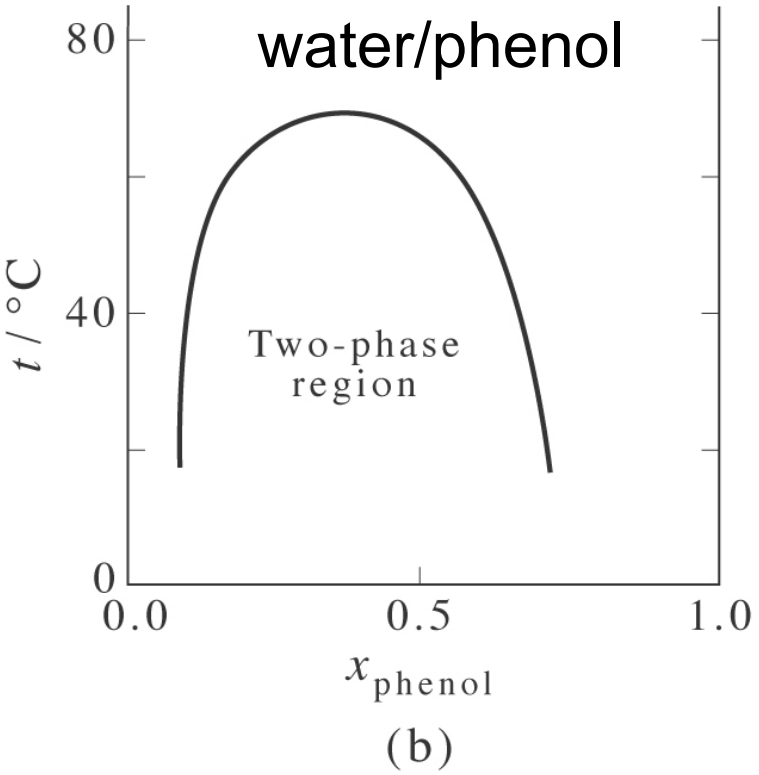
$$\left(\frac{\partial^2 P_2}{\partial x_2^2}\right) = 0$$

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:

$$\frac{n'}{n''} = \frac{n'_1 + n'_2}{n''_1 + n''_2} = \frac{x''_2 - x_2}{x_2 - x'_2}$$

Next: Regular Solutions