Statistical Molecular Thermodynamics

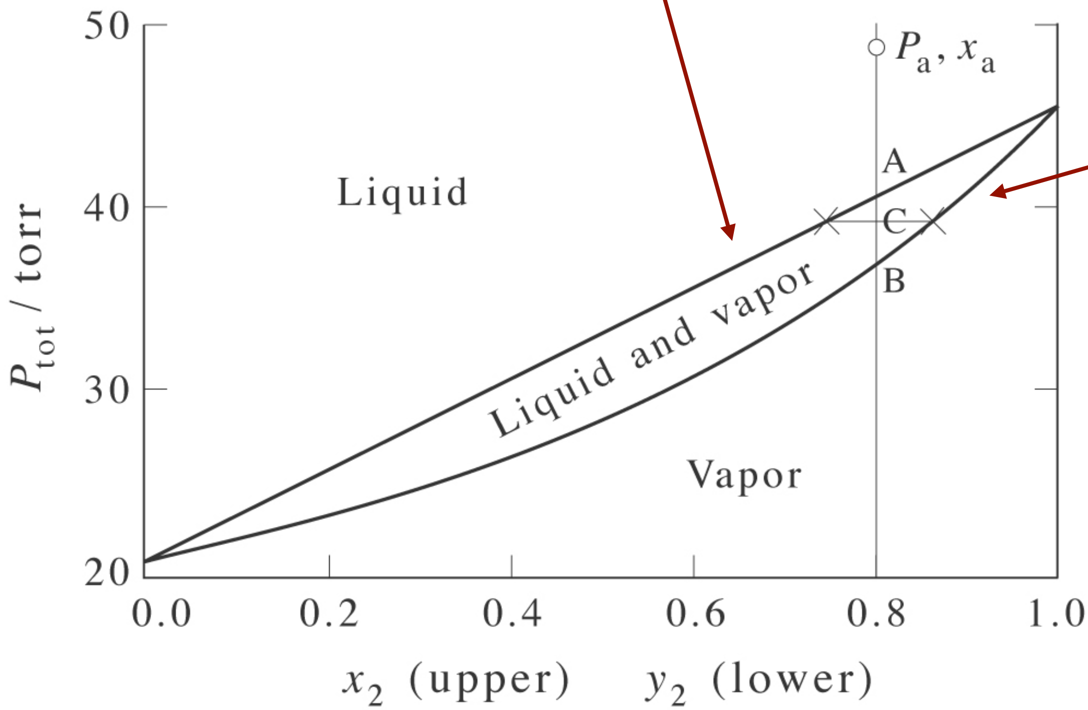
Christopher J. Cramer

Video 10.5

Ideal Solutions II

Solution Liquid-Vapor Transitions

Total VP as a function of the composition of the solution — linear for ideal solution — apply higher *pressure, only liquid phase present*



1-propanol/2-propanol at 25 °C

Pressure-composition diagram

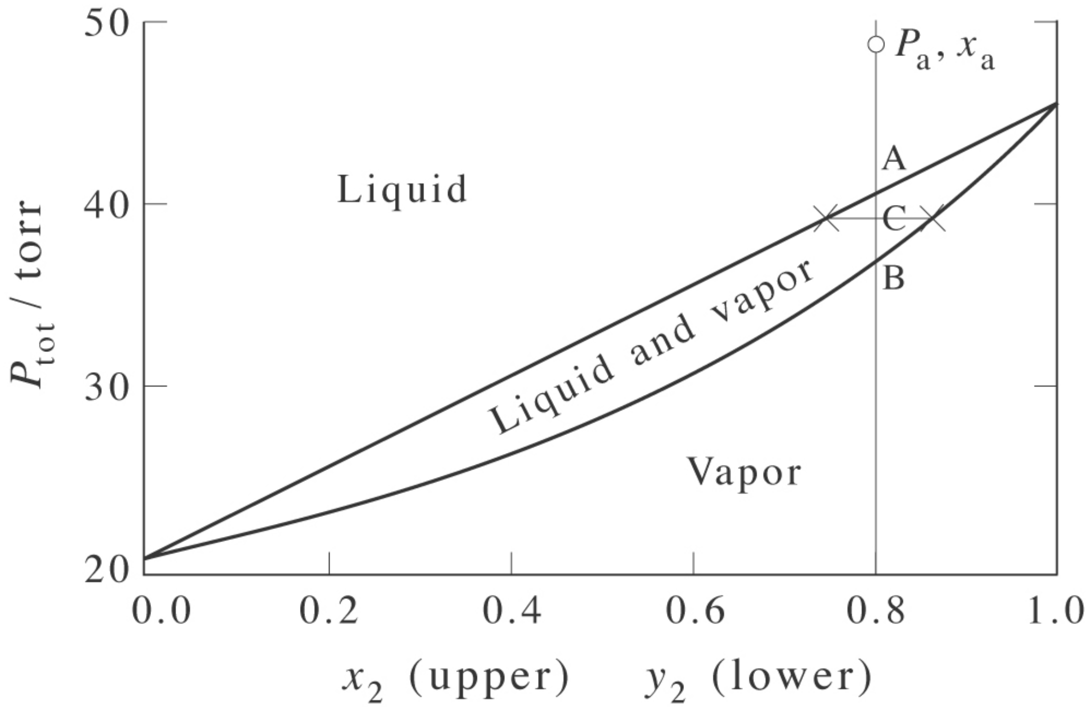
Total VP as a function of the composition of the vapor. From Laws of Dalton and Raoul:

$$y_2 = \frac{P_2}{P_{\text{total}}} = \frac{x_2 P_2^*}{P_{\text{total}}}$$

Of course, there's only a *single* pressure; the vapor is enriched in the lower boiling component compared to the higher until *all* is vapor at low *P*

Self-assessment

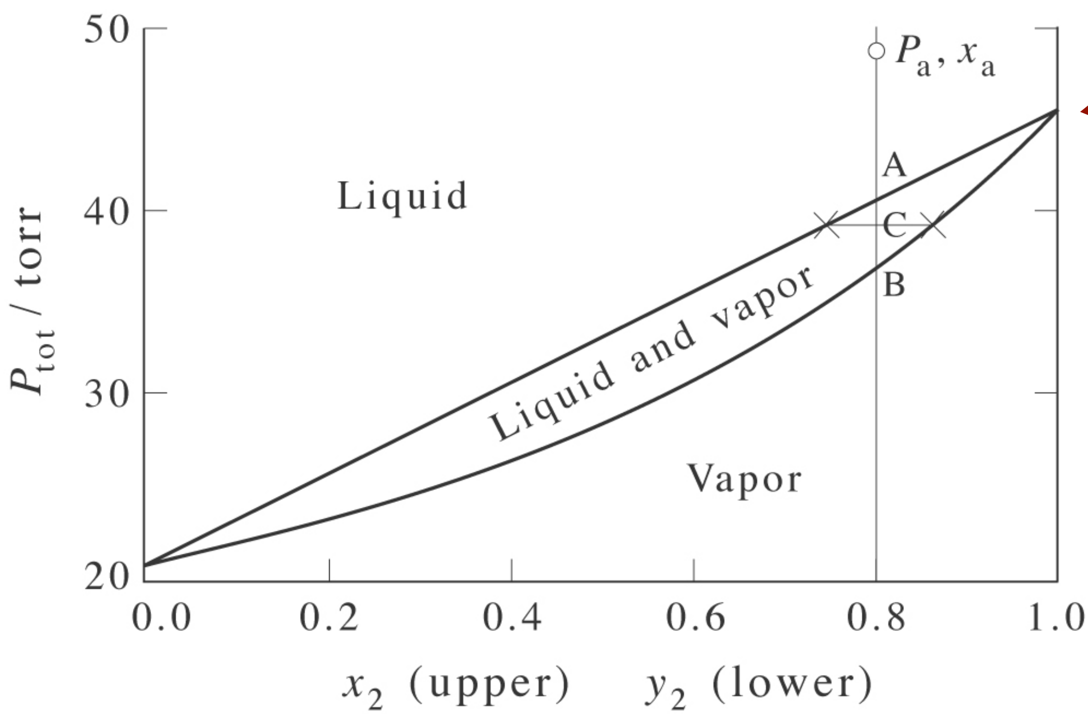
Explain the relationship between y_2 and x_2 in words, and especially, why is the former to the right of the latter given the dictates of Dalton's and Raoult's Laws?



$$y_2 = \frac{P_2}{P_{total}} = \frac{x_2 P_2^*}{P_{total}}$$

Self-assessment Explained

P_2* must always exceed P_{total} unless the liquid is pure phase 2, so y_2 will always be to the right of x_2. And, the ratio of P_2* to P_{total} will be *greatest* when the solution is nearly pure component 1 (i.e., P_{total} will be nearly P_1*). So, the y_2 curve angles sharply away from the x_2 curve at the outset, but ultimately rejoins it at the stage of pure liquid 2.



P_2*

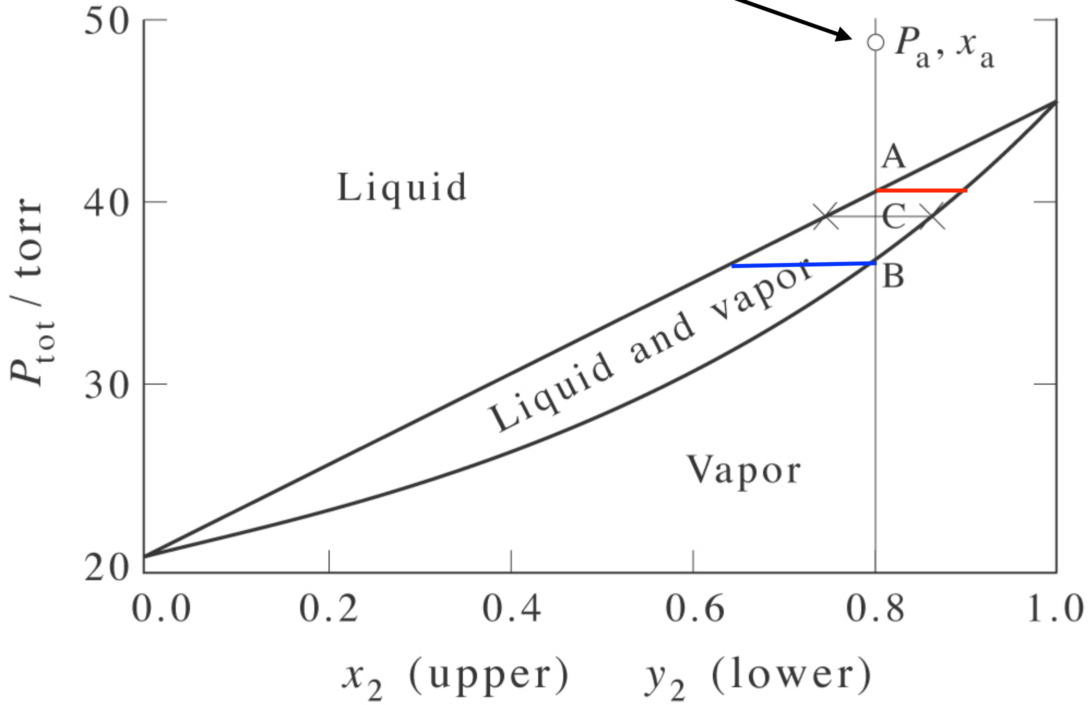
$$y_2 = \frac{P_2}{P_{\text{total}}} = \frac{x_2 P_2^*}{P_{\text{total}}}$$

It's also helpful to think about case where $x_1 = x_2 = 0.5$ and P_1 vs P_2* to understand how vapor is enriched in higher boiling component*

Vaporizing the Liquid Solution

Consider a specific composition, 0.2:0.8 *n*-PrOH:*i*-PrOH

Begin at P = 50 torr (no vapor), start pulling vacuum...



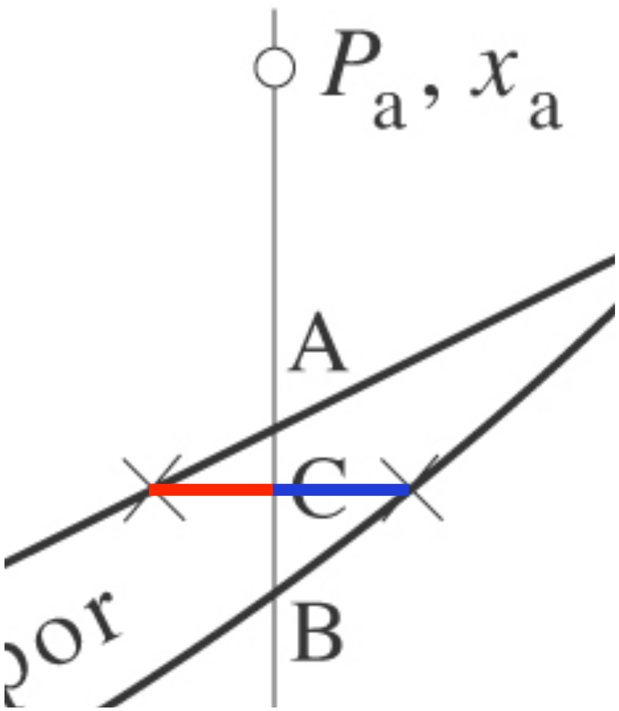
1-propanol/2-propanol at 25 °C

Pressure-composition diagram

At pressure A, the first vapor would begin to appear; it will be ~0.1:0.9 in composition, so the liquid perforce will begin to *decrease* in component 2

At pressure B, the last liquid to disappear will be ~0.35:0.65 in composition, and then the system will be *all* vapor with, of course, the original 0.2:0.8 composition

Zooming in on the Two-Phase Region



Consider point C, which lies on a line connecting the composition of the liquid (x_2 = 0.75) and vapor (y_2 = 0.87). This line is called a tie-line. Remember that the overall *system* composition (i.e., liquid *and* vapor) is x_a = 0.80

The total moles of liquid and of vapor can be determined from the *Lever Rule*

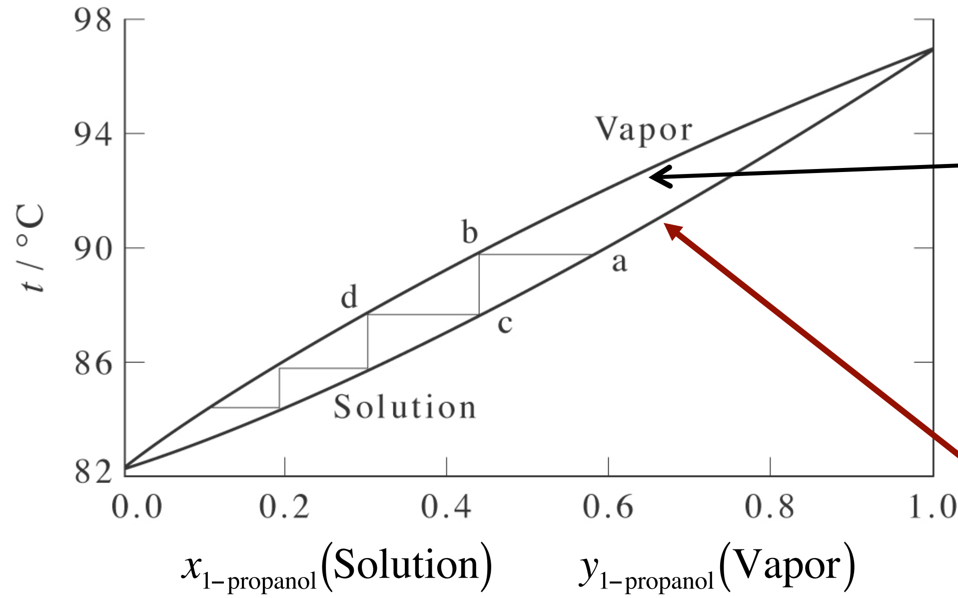
The *total* mole fraction that is liquid (x^l):

$$\frac{n^l}{n^v} = \frac{y_2 - x_a}{x_a - x_2} =$$

$$x^l =$$

Fractional Distillation

1-propanol/2-propanol at 760 torr



Using Dalton's/Raoult's laws:

$$y_1 = \frac{P_1}{760 \text{ torr}} = \frac{x_1 P_1^*}{760 \text{ torr}}$$

and:

$$P_{total} = 760 \text{ torr} = P_2^* - x_1\left(P_2^* - P_1^*\right)$$

bp as a function of composition

So, 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 <u>lower boiling</u> component at the top (the coolest point) of a distillation head!

Next: Non-ideal Solutions