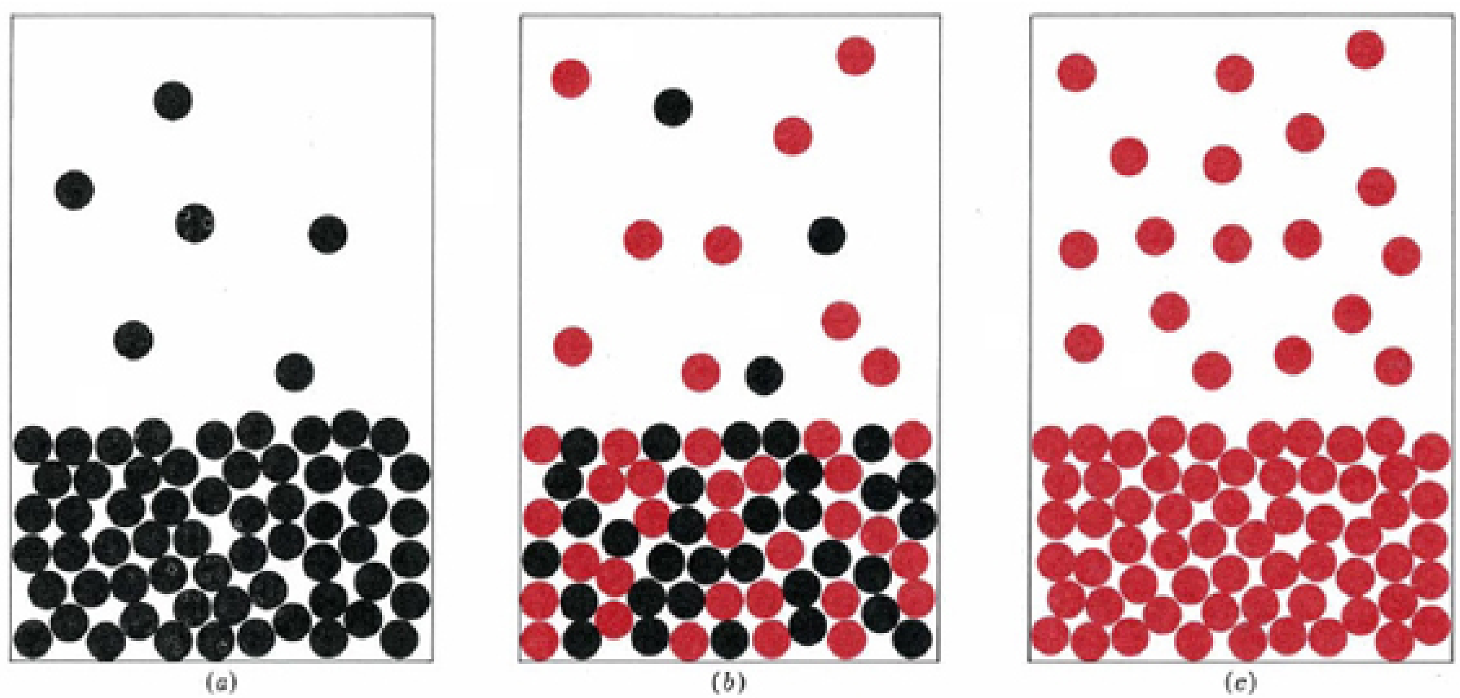
# Raoult's law

The diagram below shows two pure substances and an ideal mixture.

$P_1^*$ $\quad$ $x_1P_1^* + x_2P_2^*$ $\quad$ $P_2^*$




Less volatile $\quad$ More volatile

# Raoult’s law

We can use Raoult's law

$P_j = x_j P_j^*$

as the basis for a two-component phase diagram.
We should always keep in mind that the mole fractions of the two components are related by

$x_1 + x_2 = 1$

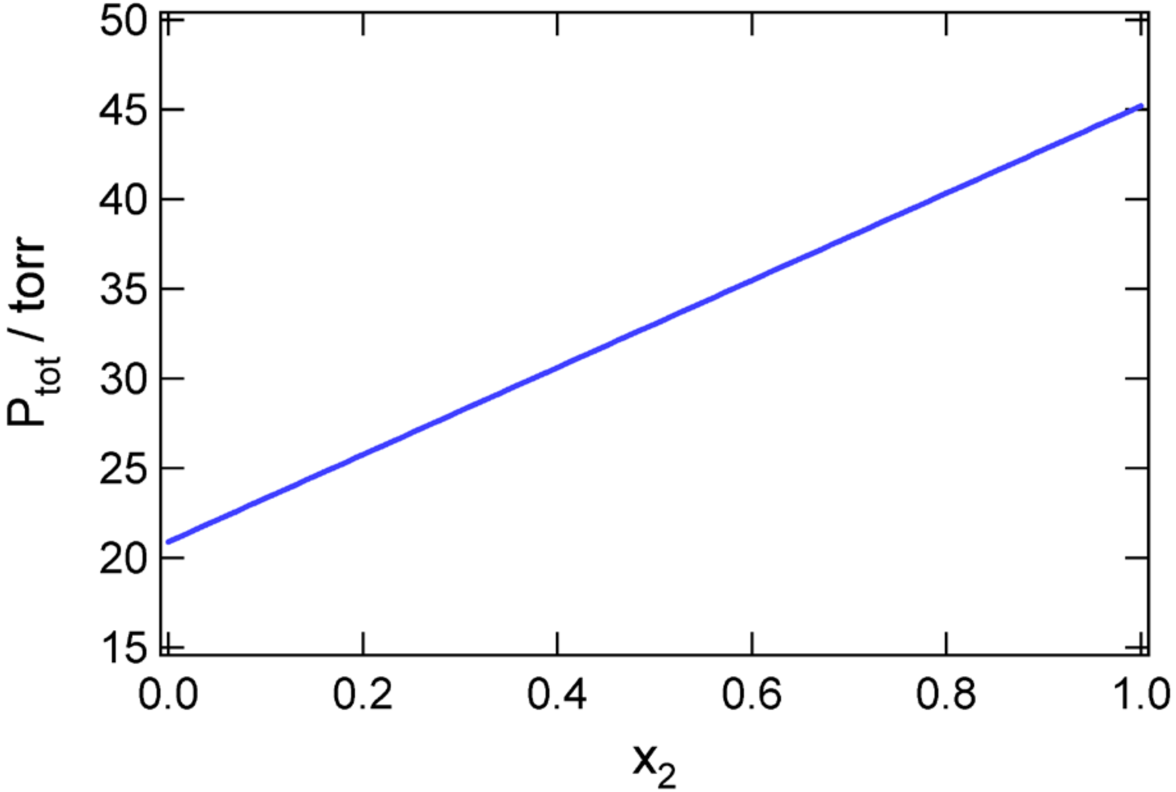
The two vapor pressures of the pure components are $P_1^*$ and $P_2^*$ .

# Two component phase diagrams

The total vapor pressure over an ideal solution is given by

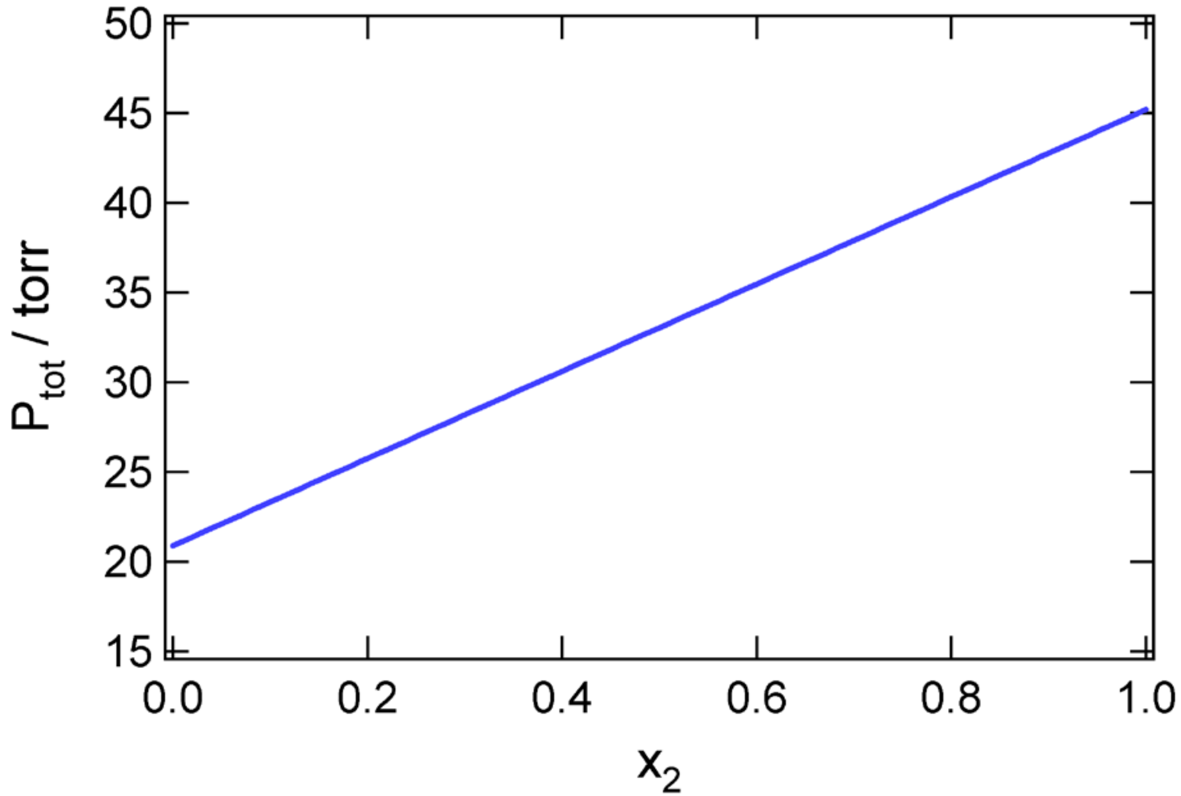
$$P_{total} = P_1 + P_2 = x_1P_1^* + x_2P_2^* = (1 - x_2)P_1^* + x_2P_2^*$$
$$= P_1^* + x_2(P_2^* - P_1^*)$$

A plot of the total pressure has the form of a straight line.



# Liquid composition: specific example

Consider the example in the book of 1-propanol and 2-propanol, which have $P_1^* = 20.9$ torr and $P_2^* = 45.2$ torr, respectively. So in this example, the phase diagram has the appearance:



# The vapor mole fraction

The value of the mole fraction in the vapor is not necessarily equal to that of the liquid. In the vapor phase the relative numbers of moles is given by Dalton's law. Applying Dalton's law we find:

$$y_1 = P_1/P_{total} = x_1 P_1^*/P_{total}$$

or

$$y_2 = P_2/P_{total} = x_2 P_2^*/P_{total}$$

The vapor curve is not the same as the liquid line.

# Deriving the vapor curve

The value of the mole fraction in the vapor is not necessarily equal to mole fraction of the liquid. In general, for a two-component mixture, one component will be more volatile than the other. In that case, the larger vapor pressure gives rise to a large mole fraction for the more volatile component. In a mixture of ethanol and water, the ethanol is more volatile. Therefore, the mole fraction of ethanol in the vapor above the liquid will be richer in ethanol than in water. To make this quantitative we can apply Dalton's law to find:

$$y_1 = \frac{P_1}{P_{total}} = \frac{x_1 P_1^*}{P_{total}} \quad \text{and} \quad y_2 = \frac{P_2}{P_{total}} = \frac{x_2 P_2^*}{P_{total}}$$

# Deriving the vapor curve

The vapor curve is not the same as the liquid line. Using the equation of the liquid line we find:

$$x_2 = \frac{P_{total} - P_1{}^*}{P_2{}^* - P_1{}^*}$$

when substituted into $y_2 = x_2 P_2{}^*/P_{total}$ we have

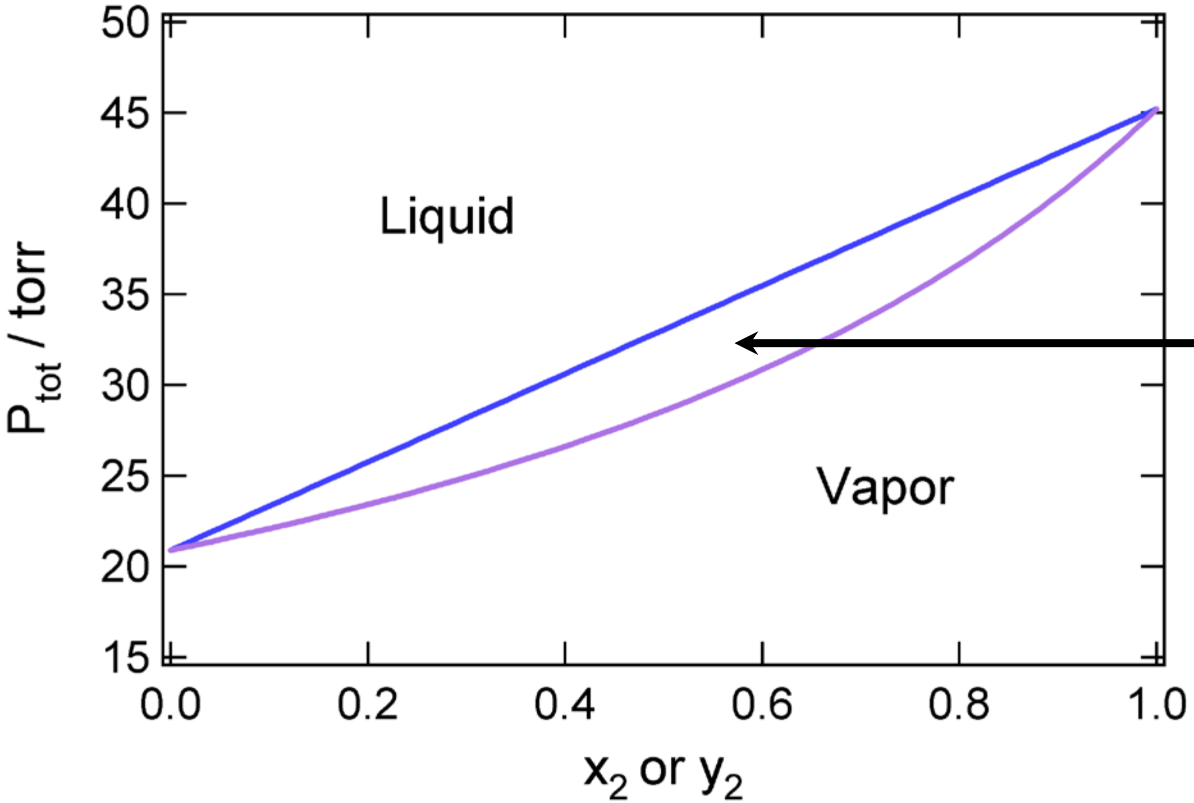
$$y_2 = \frac{P_2{}^*}{P_{total}}\left(\frac{P_{total} - P_1{}^*}{P_2{}^* - P_1{}^*}\right)$$

Solving for $P_{total}$ we find:

$$P_{total} = \frac{P_1{}^* P_2{}^*}{P_2{}^* - y_2\left(P_2{}^* - P_1{}^*\right)}$$

# The vapor curve

The is shown in the Figure below. The purple line was calculated using the Dalton's law expression. What lies between the blue and purple lines? This is the two phase region.




Two Phase Region

# The tie line

A tie line connects the two phase boundaries in a two-phase region. We show a tie line for the mole fraction $x_2 = 0.5$ on the phase diagram below.