

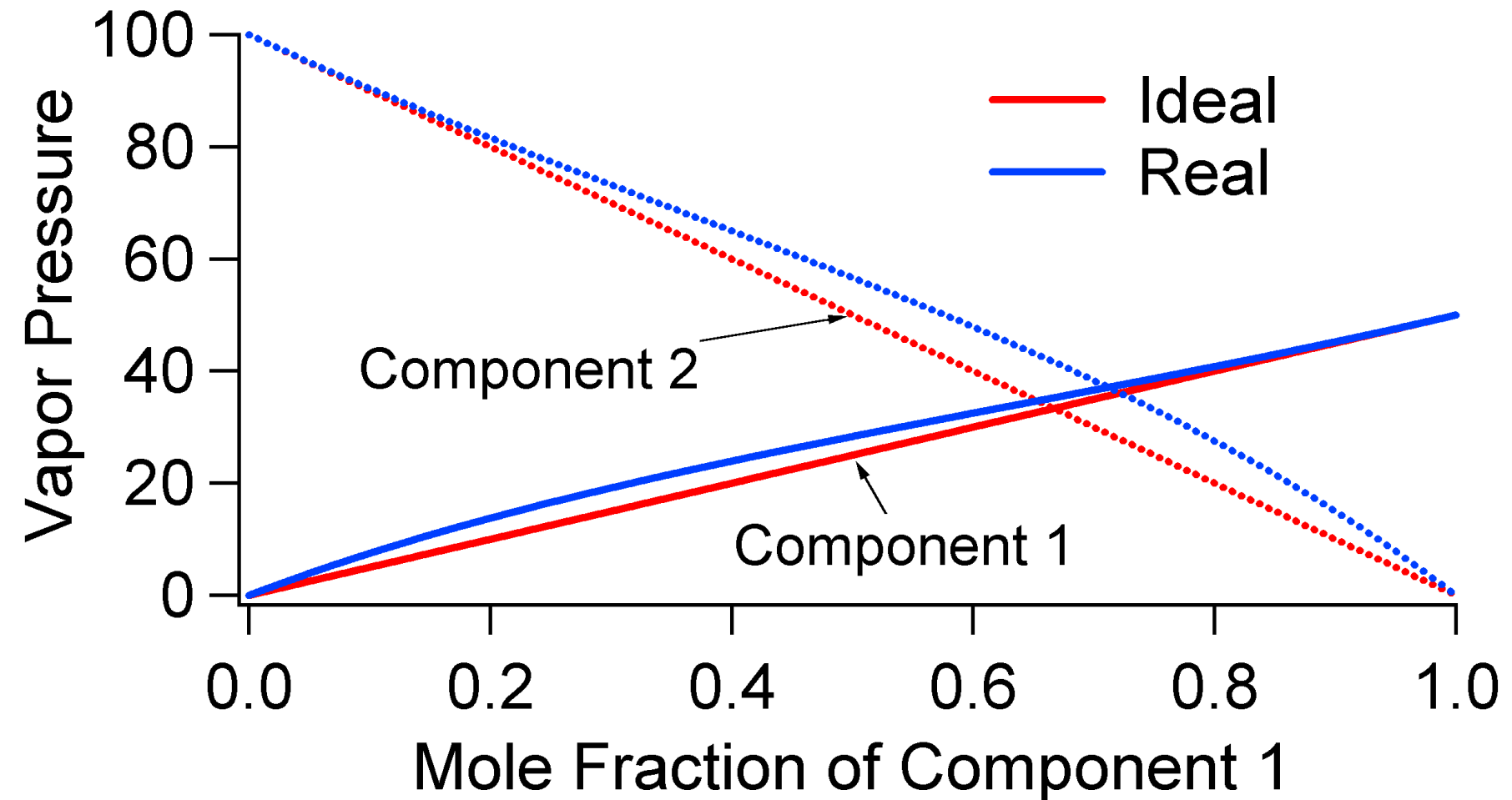
A model of molecular interactions

We can express the behavior in real solutions as a deviation from Raoult's law. For example, in the figure below we have component 1 with a vapor pressure of 50 torr for the pure component.

That is, $P_1^* = 50$ torr. Likewise, $P_2^* = 100$ torr.

We can consider two cases. Deviations from Raoult's law can be positive or negative. Positive deviations (i.e. greater vapor pressure than ideal) mean that the unlike molecules have a repulsive interaction.

Positive deviations from Raoult's law



A mathematical model for the deviations from ideality

To obtain the plots we use the following expressions.

$$P_1 = x_1 P_1^*$$

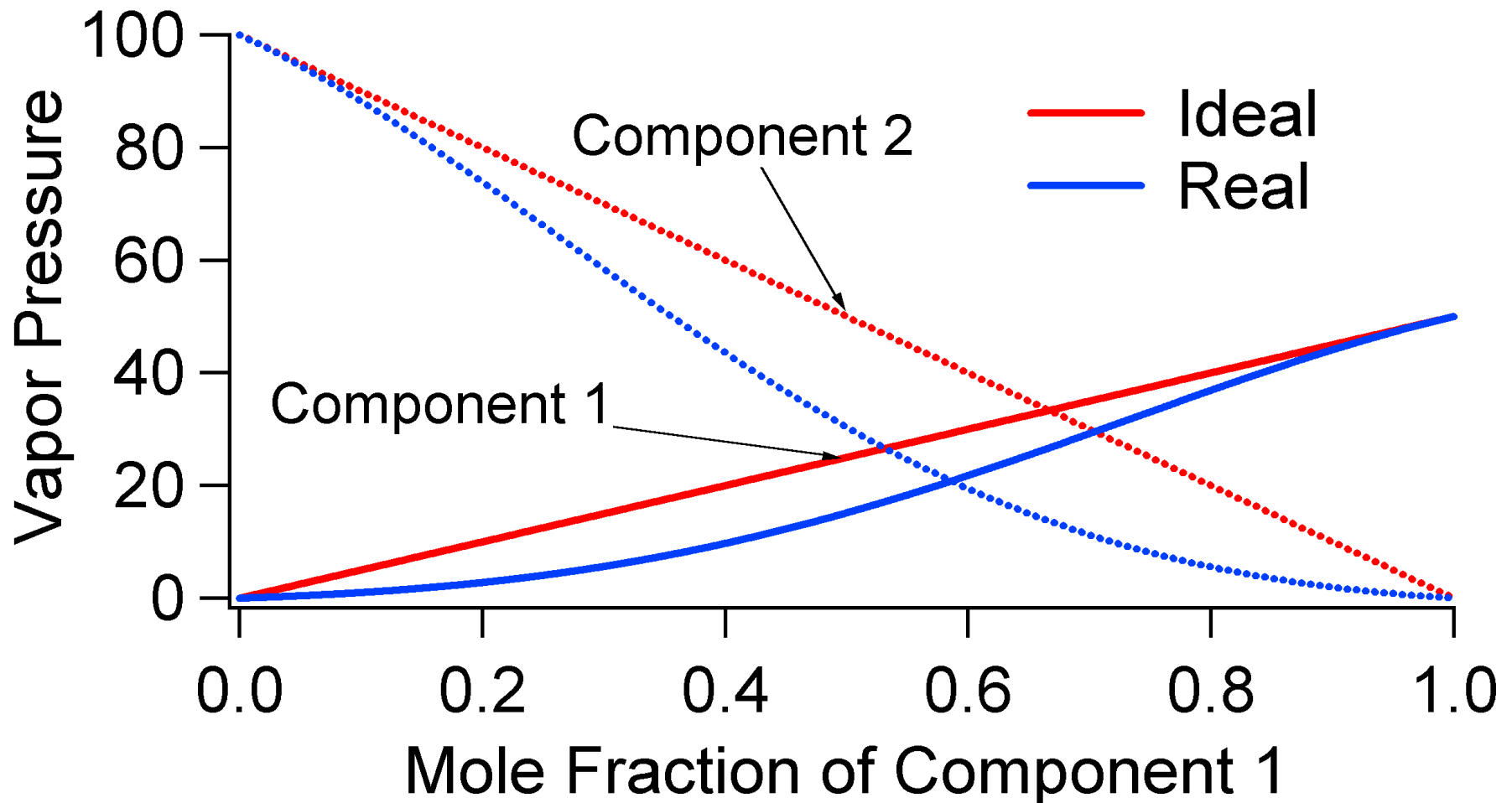
$$P_2 = x_2 P_2^*$$

$$P_1 = x_1 P_1^* \exp(\alpha x_2^2)$$

$$P_2 = x_2 P_2^* \exp(\alpha x_1^2)$$

where the term $\exp(\alpha x_2^2)$ represents a deviation from ideality ($\alpha = 0.5$ in the plot above). Negative deviations from Raoult's law are also observed as shown in the plot below ($\alpha = -2$ in the plot below).

Negative deviations from Raoult's law



Limiting behavior

For either positive or negative deviations from Raoult's law, if we look at component 1 we can see that as $x_1 \rightarrow 1$ and $x_2 \rightarrow 0$ we recover Raoult's law, $P_1 = x_1 P_1^*$. In other words when 1 is the pure solvent we have nearly ideal behavior for substance 1.

However, at the opposite limit as $x_1 \rightarrow 0$ (and $x_2 \rightarrow 1$) we have, $P_1 = x_1 P_1^* \exp(\alpha)$. In this case substance 1 is the solute and it behaves non-ideally. This has been expressed as Henry's law.

Henry's law states that $P_1 = x_1 k_{H,1}$ as $x_1 \rightarrow 0$. Thus, Henry's describes the non-ideal behavior of a solute in a dilute solution.

Note that for the explicit model above we can equate

$$k_{H,1} = P_1^* \exp(\alpha).$$

Explaining activity

Throughout the entire range of concentration we can redefine activity, a_1 . Activity is an effective mole fraction. That is we can define

$$P_1 = a_1 P_1^*$$

for a real solution. Our simple model above shows that the deviation from ideality can be treated by fitting to expressions of the form $P_1 = x_1 P_1^* \exp\{\alpha x_2^2 + \beta x_2^3 + \dots\}$

The chemical potential for this type of solution is

$$\mu_1 = \mu_1^* + RT \ln x_1 + \alpha RT x_2^2 + \beta RT x_2^3$$

We see from the definition of activity as $a_1 = P_1/P_1^*$ that we can express the chemical potential as $\mu_1 = \mu_1^* + RT \ln a_1$

Thus we can see that $a_1 = x_1 \exp\{\alpha x_2^2 + \beta x_2^3 + \dots\}$.

The activity coefficient

We can define an activity coefficient γ_1 such that

$$\gamma_1 = a_1/x_1.$$

$$\text{Therefore } \gamma_1 = \exp\{\alpha x_2^2 + \beta x_2^3 + \dots\}.$$

Clearly, $a_1 \rightarrow x_1$ and $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$. Thus, the solution approaches ideal behavior as the composition approaches that of the pure solution. This definition is based on a Raoult's law standard state. This is also known as a solvent standard state.

The activities or chemical potentials are meaningless unless we know the standard state. The solvent or Raoult's law standard state holds for substances that are miscible in all proportions.

$$\mu_1 = \mu_1^* + RT \ln a_1$$