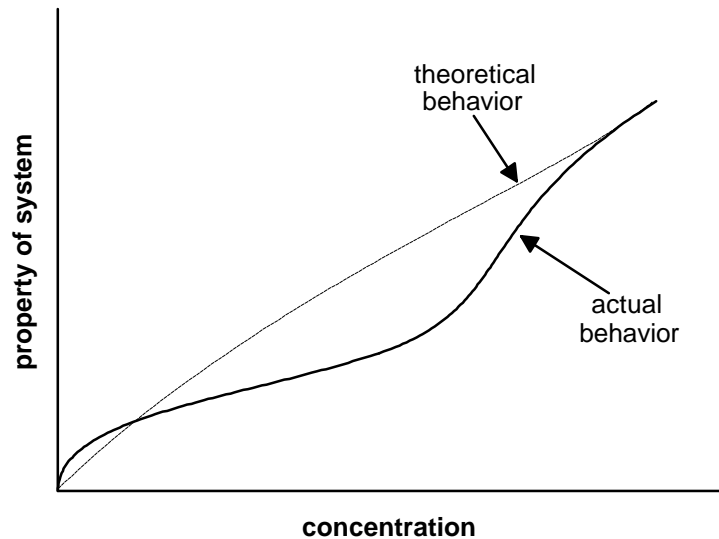


What is Activity?

The concept of *activity* can be used whenever there is a difference between *ideal* and *observed* properties as a function of concentration. For example, in the following figure, the dashed line shows the predicted behavior of a system as a function of concentration according to some simplified model, while the solid line represents the actual (i.e., observed) behavior as the system composition changes.



In most cases, the observed and predicted behaviors will approach one another asymptotically at either low concentrations (“infinite dilution”) or high concentrations (“pure solute”). In the previous figure, for example, theory and experiment are asymptotic at high concentrations. Theoretical constructs that exhibit this behavior are sometimes called *limiting laws*.

The activity of a component in a mixture is a way of describing the actual behavior of the system in terms of its model behavior. It is the “effective concentration” of a component of the system, according to some idealized picture of how the system ought to act.

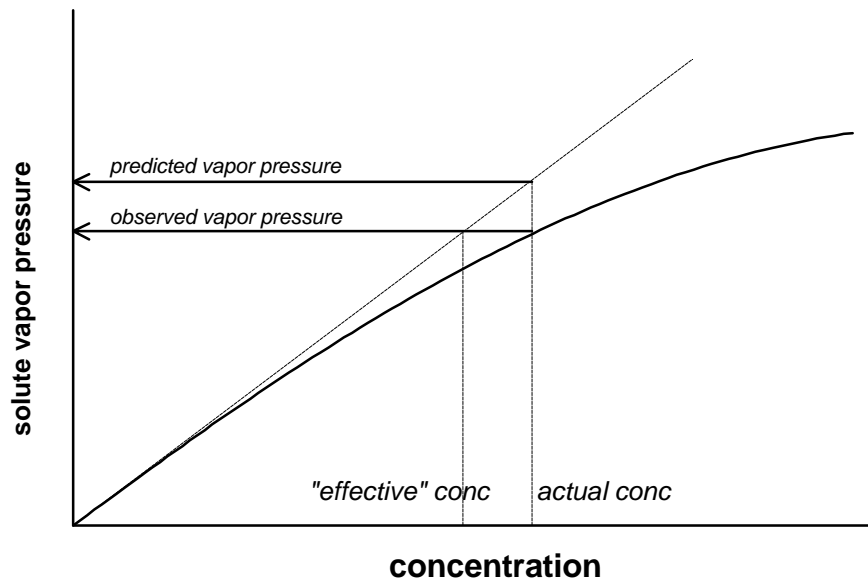
The Activity of Solutes in Solutions

In order to use activity, we must have some sort of model of ideal behavior; our model will be that of an *ideal dilute solution*, which is defined as a solution that follows **Henry's Law**:

definition of an ideal dilute solution $p_A = K_H[A]$

where p_A is the partial vapor pressure of the solute above the solution, $[A]$ is the concentration of the solute in the solution, and K_H is a constant (*Henry's constant*). Note that Henry's constant is often used to express the solubilities of gases in liquids.

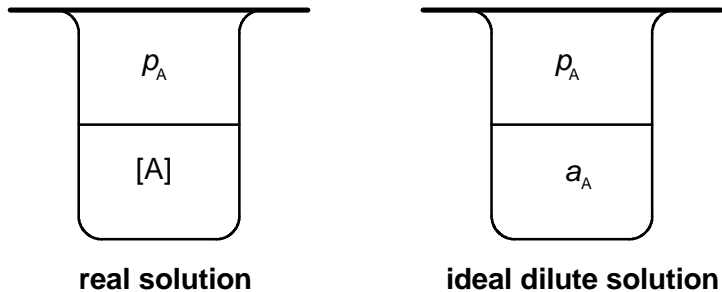
In order for a solution to follow Henry's Law, it must possess the following characteristic: **the solute is surrounded on all sides by solvent molecules**. Most solutions approximate this ideal only at dilute concentrations (hence the name "ideal dilute solutions"), as shown in the following figure.



An ideal dilute solution of concentration $[A]$ would be expected to exert a vapor pressure as predicted by Henry's Law. In most cases, the observed vapor pressure will be some different value, the difference being due to the departure of the actual solution from the characteristics in an ideal dilute solution. The departure from ideal behavior can be expressed as the ratio of observed and ideal behaviors; this ratio, γ , is the **activity coefficient** of the solute.

$$\gamma_A = \frac{\text{observed vapor pressure}}{\text{predicted (ideal) vapor pressure}}$$

Let's imagine that a given solution of concentration $[A]$ exerts a pressure of p_A ; an *ideal dilute solution* of concentration a_A would give the **same** vapor pressure:



In other words, the activity is the concentration of solute that would be needed to exert vapor pressure p_A if the solution possessed the properties of an ideal dilute solution. Another way of looking at it is that the solution of concentration $[A]$ “acts like” an ideal solution of concentration a_A . The activity is the “effective concentration” of the real solution, where the term “effective” refers specifically to the behavior of some ideal (in this case, a solution that follows Henry’s Law).

Since Henry’s Law is linear with concentration, the activity coefficient is also the ratio of the activity to the actual concentration:

$$\gamma_A = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a_A}{[A]}$$

In other words, the activity can be calculated if the activity coefficient is known.

activity of solute A

$$a_A = \gamma_A[A]$$

The activity coefficient indicates the extent of the departure of the solute from ideal behavior.

Our model of an ideal solute is one in which every solute molecule is surrounded only by solvent molecules. This picture is more closely approached as the concentration decreases – Henry’s Law is a limiting law that is approached asymptotically as the concentration approaches zero. Thus, as $[A] \rightarrow 0$, then $\gamma_A \rightarrow 1$ and $a_A \rightarrow [A]$, as seen in the previous figure.

One final note: the **standard state of a solution** is defined as an *ideal dilute* solution ($\gamma = 1$) in which the concentration of the solute is 1 M. Put more succinctly, the standard state of a solute in solution is when the solute activity is 1 M.