Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 11.2

Concentrations and Standard States

Standard States
Compare and Contrast
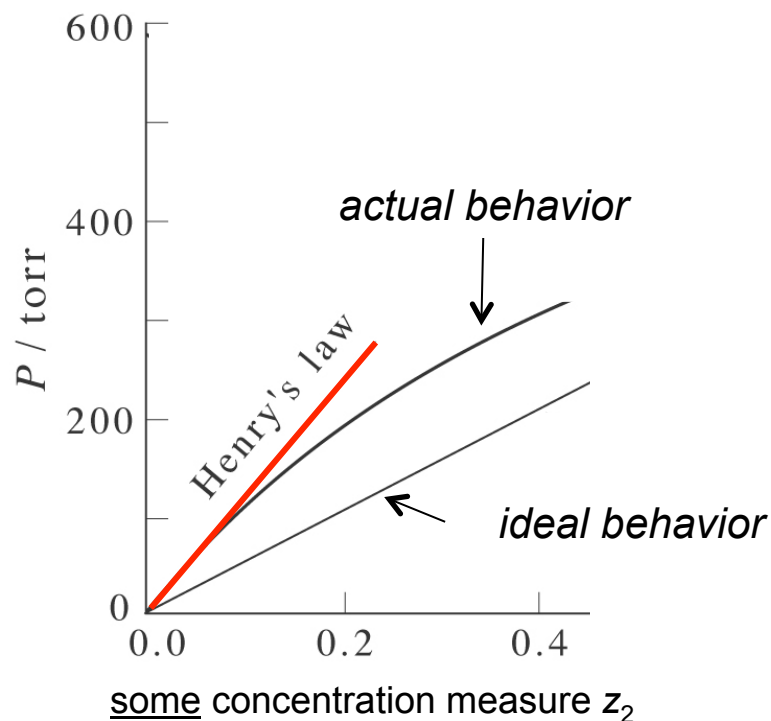
Solvent (1): *always mole fraction (x_1), always Raoult's law*

$$a_1 = \frac{P_1}{P_1^*} \quad \Rightarrow \quad \gamma_1 = \frac{a_1}{x_1} \qquad a_1 \underset{\lim x_1 \to 1}{\to} x_1 \quad \left(\text{or} \quad P_1 \underset{\lim x_1 \to 1}{\to} x_1 P_1^* \right)$$

Solute (2): *different options, but always Henry's law*

mole fraction	molality	molarity

$$a_{2x} = \frac{P_2}{k_{H,x}} \qquad a_{2x} \underset{\lim x_2 \to 0}{\to} x_2$$

$$\gamma_{2x} = \frac{a_{2x}}{x_2} \qquad P_2 \underset{\lim x_2 \to 0}{\to} x_2 k_{H,x}$$

$$a_{2m} = \frac{P_2}{k_{H,m}} \qquad a_{2m} \underset{\lim m \to 0}{\to} m$$

$$\gamma_{2m} = \frac{a_{2m}}{m} \qquad P_2 \underset{\lim m \to 0}{\to} m k_{H,m}$$

$$a_{2c} = \frac{P_2}{k_{H,c}} \qquad a_{2c} \underset{\lim c \to 0}{\to} c$$

$$\gamma_{2c} = \frac{a_{2c}}{c} \qquad P_2 \underset{\lim c \to 0}{\to} c k_{H,c}$$

# WHAT *Is* HENRY'S CONSTANT?

some concentration measure z_2

Henry's constant has units of pressure per Ω, where Ω represents the units for z_2.

And, if we consider the special case of $z_2 = 1$, we see that Henry's constant is the vapor pressure that would be observed for a solution having concentration of 1 Ω but behaving as though it were infinitely dilute. That's a hypothetical situation, but a useful one.

$$P_2 \to z_2 k_{H,z} \text{ as } z_2 \to 0$$

The *Henry's law constant* reflects the intermolecular interactions between the solute when surrounded entirely by solvent (infinite dilution).

WHAT *IS* ACTIVITY?
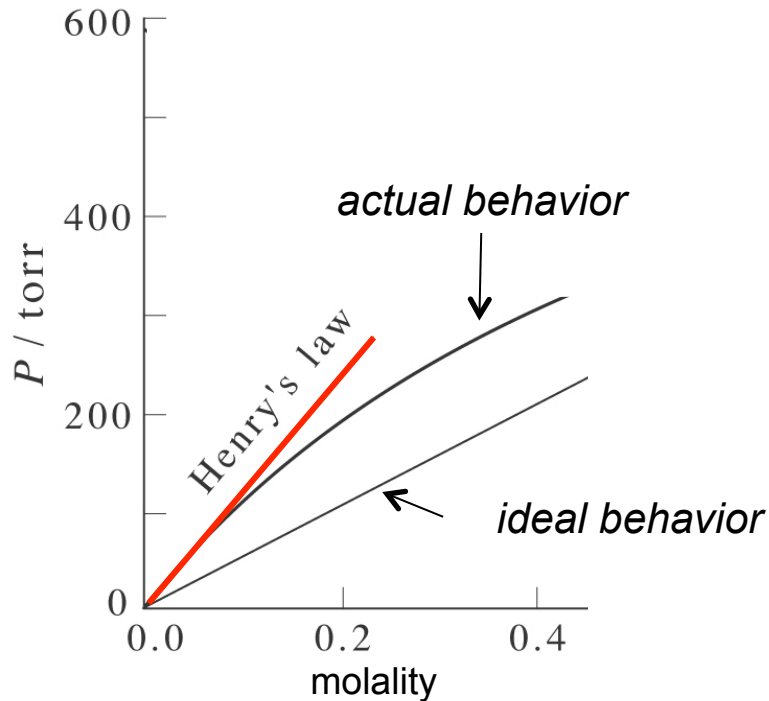
Deviation of activity from the Ω concentration (measured by an activity coefficient γ different from 1) reflects the degree to which the solute would like to *leave* or *stay* in solution, compared to what would be expected based on its infinitely dilute behavior. An activity coefficient *greater* than 1 implies a desire to *leave* (higher gas pressure than expected), an activity coefficient *less* than 1 implies a desire to *stay* (lower gas pressure than expected).
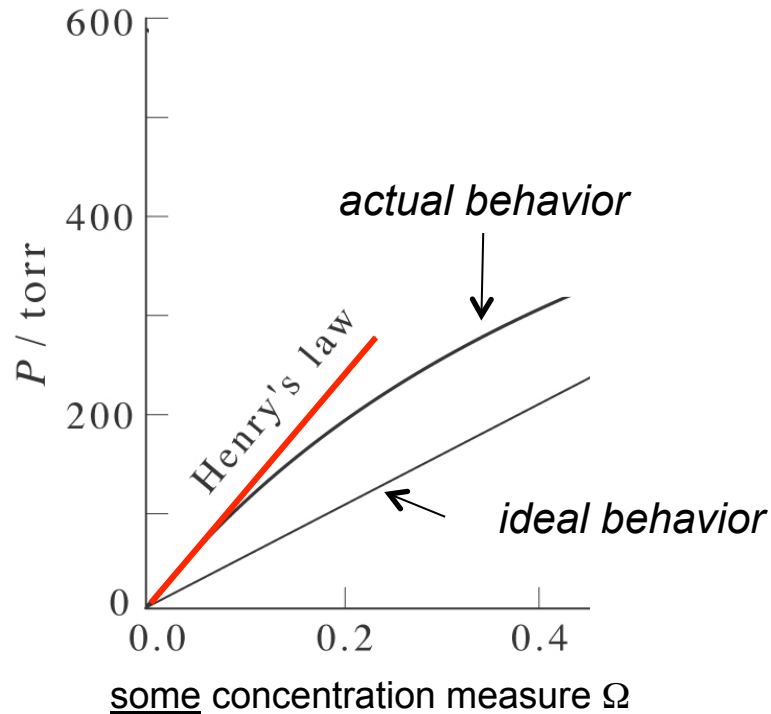
$$a_{2m} = \frac{P_2}{k_{H,m}} \qquad a_{2m} \underset{\lim m \to 0}{\longrightarrow} m$$

$$\gamma_{2m} = \frac{a_{2m}}{m} \qquad P_2 \underset{\lim m \to 0}{\longrightarrow} m k_{H,m}$$

molality example

In the example here, $\gamma_{2m} \leq 1$ over the indicated range.

Self-assessment

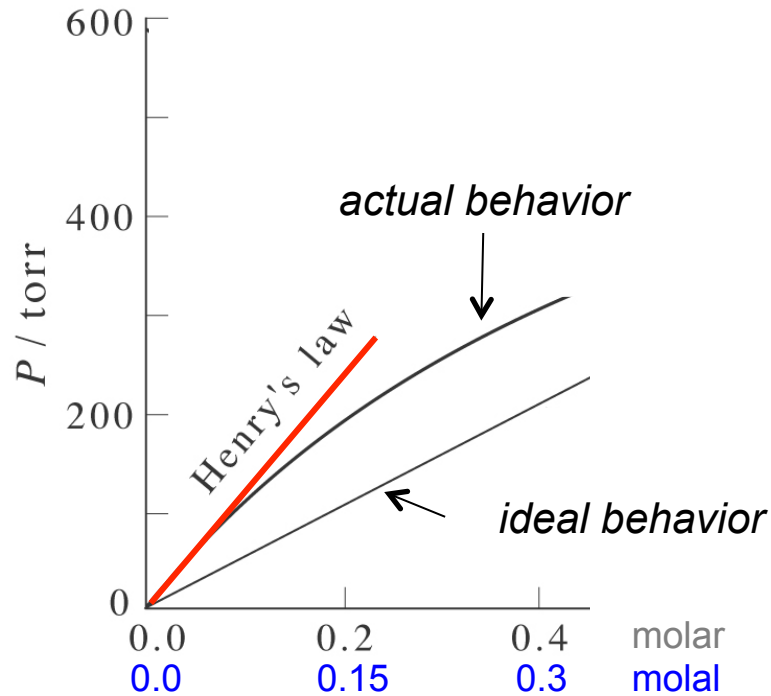some concentration measure Ω

A solute is dissolved in a solvent that has a density of greater than 1 g/mL and there is no change in volume upon mixing. Pressure/concentration behavior like that shown at right is observed. Will a measured activity be larger in the molal standard state, or in the molar standard state?

$$a_{2m} = \frac{P_2}{k_{H,\Omega}} \qquad a_{2\Omega} \underset{\lim \Omega \to 0}{\longrightarrow} \Omega$$

$$\gamma_{2\Omega} = \frac{a_{2\Omega}}{\Omega} \qquad P_2 \underset{\lim \Omega \to 0}{\longrightarrow} \Omega k_{H,\Omega}$$

Self-assessment Explained

$$a_{2m} = \frac{P_2}{k_{\mathrm{H},\Omega}} \qquad a_{2\Omega} \xrightarrow[\lim \Omega \to 0]{} \Omega$$

$$\gamma_{2\Omega} = \frac{a_{2\Omega}}{\Omega} \qquad P_2 \xrightarrow[\lim \Omega \to 0]{} \Omega k_{\mathrm{H},\Omega}$$

Since the solvent has a density of greater than 1 g/mL and there is no change in volume upon mixing, the molarity must be greater than the molality. Thus, if we plotted *both* concentration measures against P, it might appear as shown at left (for a density of 1.33 g/mL, for example). The slope of the Henry's Law line must therefore be *larger* in the molal standard state than in the molar standard state. As that slope is k_{H} for the corresponding state, activity will be *smaller* in the molal standard state for a given, observed P_2.

Next: Determining Solute Activity