

Henry's law

Attractive interactions between unlike molecules leads to negative deviations from Raoult's law (lower vapor pressure than ideal) and repulsive interactions lead to positive deviations (higher vapor pressure than ideal).

As any solution approaches a mole fraction of one (i.e. approaches a pure solution of one component) it becomes an ideal solution. In other words, $P_1 \rightarrow x_1 P_1^*$ as $x_1 \rightarrow 1$. However, as $x_1 \rightarrow 0$ the component is surrounded by unlike molecules and the solution has the maximum deviation from ideal behavior. For this case we define Henry's law, $P_1 \rightarrow x_1 k_{H,1}$ as $x_1 \rightarrow 0$. In this expression $k_{H,1}$ is the Henry's law constant. Although we have focused on component 1 the same holds true for component 2.

Henry's law

The statement of Henry's law is:

$$P_1 = x_1 k_{H,1}$$

It looks like Raoult's law except that you have this funny constant $k_{H,1}$ instead of P_1^* (the vapor pressure of component 1). This law is only valid for dilute solutions, i.e. when component 1 is the solute. Under these conditions the vapor pressure of component 1 really does not matter, because component 1 is mostly surrounded by component 2 and so its properties really quite different from the properties of pure 1.

Henry's law can be applied to mixtures of solvents And also to solutions of gases in liquids. For example, see the problems on the concentration of O_2 and N_2 in water at the end of the lecture.

Henry's law constant and the solubility of gases

Henry's law constants in H₂O
(atm x 10³)

He	131
N ₂	86
CO	57
O ₂	43
Ar	40
CO ₂	1.6

Problem: Divers get the bends if bubbles of N₂ form in their blood because they rise too rapidly. Calculate the molarity of N₂ in water (i.e. blood) at sea level and 100 m below sea level.

Henry's law constant and the solubility of gases

Henry's law constants in H₂O
(atm x 10³)

He	131
N ₂	86
CO	57
O ₂	43
Ar	40
CO ₂	1.6

Problem: Divers get the bends if bubbles of N₂ form in their blood because they rise too rapidly. Calculate the molarity of N₂ in water (i.e. blood) at sea level and 100 m below sea level.

$$\text{At sea level: } x_{\text{N}_2} = P_{\text{N}_2} / k_{\text{H,N}_2} = 0.8 \text{ atm} / 86 \times 10^3 \text{ atm} = 9.3 \times 10^{-6}$$
$$c_{\text{N}_2} = 55.6 x_{\text{N}_2} = 5 \times 10^{-4} \text{ mol/L}$$

$$\text{At 100 m: } x_{\text{N}_2} = P_{\text{N}_2} / k_{\text{H,N}_2} = 7.84 \text{ atm} / 86 \times 10^3 \text{ atm} = 8.8 \times 10^{-5}$$
$$c_{\text{N}_2} = 55.6 x_{\text{N}_2} = 4.8 \times 10^{-3} \text{ mol/L}$$

A note on conversion from mole fraction to molarity

The conversion from mole fraction to molarity can be solved analytically. We begin with the proportionality:

$$\frac{c_2}{c_1} = \frac{x_2}{x_1}$$

Which leads to

$$c_2 = c_1 \frac{x_2}{x_1} \approx c_1 x_2$$

Note that for water as solvent (component 1) $x_1 \sim 1$ and the Concentration of water is $c_1 \sim 55.6$ so that the conversion For a dilute solute such as a gas is $c_2 \sim 55.6 x_2$

The Henry's law constant is an equilibrium constant

Gases dissolve in liquids to form solutions. This dissolution is an equilibrium process for which an equilibrium constant can be written. For example, the equilibrium between oxygen gas and dissolved oxygen in water is $O_2(aq) \rightleftharpoons O_2(g)$. The equilibrium constant for this equilibrium is:

$$K'_H = \frac{P_{O_2}}{c_{O_2}}$$

The form of the equilibrium constant shows that **the concentration of a solute gas in a solution is directly proportional to the partial pressure of that gas above the solution.**

The Henry's law constant is tabulated for c and x

The Henry's law constant can be tabulated for mole fraction (as seen in the previous problem) or for molarity. If the units of the Henry's law constant are 'atm' then it is valid for mole fraction. If the units are 'atm/(mol/L)' then K'_H is tabulated for molarity. The relationship between the two is:

$$K_H = K'_H c_{H_2O}$$

Since the concentration of water is $c(H_2O) = 55.55$ molar.

$$K_H = K'_H (\text{atm } M^{-1})(55.6 M)$$

For example, K'_H is 773 atm/(mol/L) for O_2 .