University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2014

Lecture 15 8/01/14
ERD 8.12
Devoe: 9.4.4-9.4.5

A. Henry's Law

- The Henry's Law solution model is the next step up in complexity from the ideal solution. Real solutions will deviate from the linear behavior predicted for ideal solutions by Raoult's Law. See Figure 1.
- Non-ideal (i.e. real) solutions display highly non-linear and very complex behavior when the pressure above the solution is plotted as a function of mole fraction of solute x_2. However near the extremes $x_2=0$ and $x_2=1$, the curve approaches Raoult's Law behavior.
- Henry's Law is an empirical relationship that is applicable to very dilute solutions.

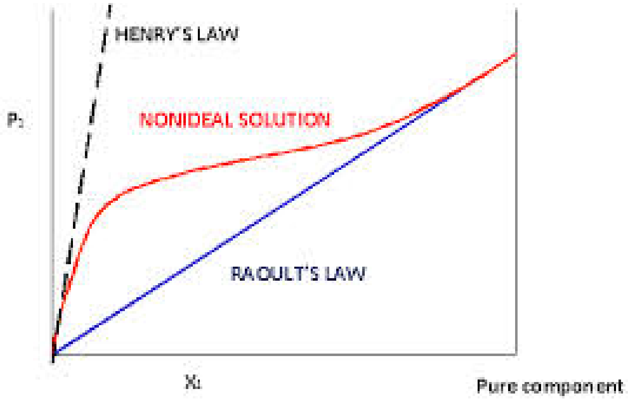

Figure 1: graphical illustration of Henry's Law behavior for a non-ideal solution versus an ideal solution.

- At high dilution of solute (x_2<<1) the solvent of a Henry's Law solution obeys Raoult's Law. This is because solvent molecules largely interact with other solvent molecules…producing virtually ideal solution conditions.
- But note that if we extrapolate the Henry's Law line from the linear region to $x_2=1$ (which may or may not be a physically achievable limit), it does NOT extrapolate to P_2^*, where Raoult's Law extrapolates.
- Instead we find that Henry's law extrapolates to a constant k_i^H such that henry's Law is an empirical linear Law of the form

$$P_i = k_i^H x_i \tag{14.1}$$

- T find out the relationship between the Henry's Law constant and the chemical potential, assume the vapor of the solute behaves ideally and is in equilibrium with the liquid:

$$\mu_2(v) = \mu_2^0 + RT\ln\left(P_2 / P_2^*\right) = \mu_2(\ell) \tag{14.2}$$

- The problem we encounter is encountered in defining the chemical potential of the pure solute. In the case of ideal solutions we assumed:

$$\mu_2^*(\ell) = \mu_2^0 + RT\ln\left(\frac{P_i}{P_i^*}\right) \tag{14.3}$$

- Note for ideal solutions the reference states of $\mu_2(\ell)$ and $\mu_2^*(\ell)$ are the same.

  But for a Henry's Law solution where the solute might be a gas or a solid in pure form, the reference states may not be the same. Assume this is the case. The chemical potential has the form:

$$\mu_2(\ell) = \mu_2^{\otimes} + RT\ln x_2 \tag{14.4}$$

  - The standard state chemical potential in equation 14.4 corresponds to a dilute solution where every solute molecule is surrounded by solvent molecules. To get the Henry's Law constant, we extrapolate x2 to high vlues but clearly...unlike the standard states of an ideal solution,where the standard
  - In a Henry's Law solution the standard free energy is $\overline{G}_i^{0,dil\,so\ln}$, which is defined as the free energy of solute I at higher concentration but under conditions where it is still largely a dilute solution. Note that unlike a ideal solution, where all components can vary from mole fractions of zero to 1, the solutes in a Henry's Law solution must remain dilute…with mole fractions near zero…
- If the vapor of a solute of a Henry's Law solution is in equilibrium with the component in solution…then

$$\mu_2(v) - \mu_2(\ell) = \mu_2^0 + RT\ln\left(P_2/P_2^*\right) - \mu_2^{\otimes} - RT\ln x_i = 0$$

$$or\ldots -\left(\mu_2^0 - \mu_2^{\otimes}\right) = +RT\ln\left(P_2/x_2P_2^*\right) \tag{14.5}$$

$$\therefore P_2 = x_2P_2^*\exp\left[\frac{-\left(\mu_2^0 - \mu_2^{\otimes}\right)}{RT}\right] = x_2k_2^H$$

where the Henry's Law constant is

$$k_2^H = P_2^*\exp\left[\frac{-\left(\mu_2^0 - \mu_2^{\otimes}\right)}{RT}\right] \tag{14.6}$$

- Equation 14.6 means the Henry's Law constant deviates from P_2^* because $\mu_2^0 - \mu_2^{\otimes} \neq 0$
- In a Henry's Law solution the solvent often behaves ideally because it is in high abundance. However it is possible for both components to follow Henry's Law in the dilute limit, as shown in Figure 2:

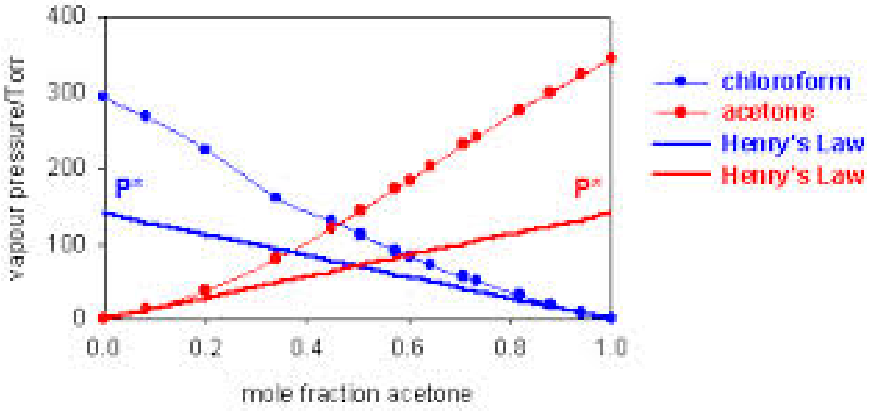

Figure 2: Henry's Law behavior for a mixture of acetone and chloroform.

- Example: Henry's Law is the basis for the alcohol breath test. Suppose a sample of breath taken from a driver has a partial pressure of ethanol is 10^{-6} atm. What is the percentage by weight of ethanol in the breath? Assume ethanol forms a Henry's Law solution in the saliva and that ehtnol in the breath is in equilibrium with ethanol in the saliva. Assume the Henry's Law constant for ethanol is 10^{-3} atm.

  Solution: Calculate the mole fraction of ethanol (EtOH) in the dilute limit… . $x_{EtOH} = \dfrac{n_{EtOH}}{n_{EtOH} + n_{water}} \approx \dfrac{n_{EtOH}}{n_{water}}$

  Convert to weight ratio:
  $$\frac{weight\ EtOH}{weight\ water} = \frac{n_{EtOH}}{n_{water}} \times \frac{46g/mole}{18g/mole} = (0.001)(2.56) = 2.56 \times 10^{-3} \Rightarrow 2.56 \times 10^{-3} \times 100\% = 0.3\%$$

  - Note: In the text Henry's law is stated in concentration units of molality m (moles solute/kg solvent)… $P_i = km$, whereas we have used the mole fraction. For dilute solutions… $\chi_{solute} \approx \dfrac{n_{solute}}{n_{solvent}} = \dfrac{n_{solute}}{(n_{solvent}/kg_{solvent})kg_{solvent}} = \dfrac{1000m}{MW(moles/g)}$. Then $P_i = k_H \chi_i = \dfrac{1000k_H}{MW} m_i = km_i$
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