

## Week 8

# Solutions

### 8.1 Vapor Pressure Lowering and Consequences

2/28:

- Colligative properties.
  - Vapor pressure lowering.
  - Boiling point elevation for non-volatile solutes.
  - Freezing point depression for solutes (excluding solids).
  - Osmotic pressure.
- **Vapor pressure lowering:** The process of adding less volatile solutes to lower the overall vapor pressure via Raoult's law.
- **Boiling point elevation:** The increase in the normal boiling point of a mixture due to vapor pressure lowering.

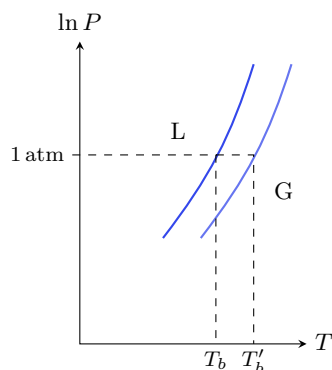


Figure 8.1: Boiling point elevation.

- In Figure 8.1, the dark blue line is the original liquid-gas coexistence curve and the light blue line is the liquid-gas coexistence curve with vapor pressure lowering — notice how at any given temperature, the corresponding pressure represented by the light blue line is lower than that given by the dark blue line.
- However, we still need to achieve a vapor pressure of 1 atm for the liquid to boil.
- We can get to such a pressure with a higher temperature, i.e., by heating the liquid to  $T'_b$  instead of just  $T_b$ .
- Calculating the change in the boiling point  $\Delta T_b$ .

- We can calculate the boiling point elevation from the Clausius-Clapeyron equation.

$$\begin{aligned}
 \frac{\Delta P}{\Delta T_b} &= \frac{\Delta \bar{H}}{T_b \Delta \bar{V}} \\
 \Delta T_b &= P^*(1-x) \frac{T_b \Delta \bar{V}}{\Delta \bar{H}} \\
 &= P^*(1-x) \frac{T_b \bar{V}_g}{\Delta \bar{H}} \\
 &= P^*(1-x) \frac{T_b R T_b}{P^* \Delta \bar{H}} \\
 &= \frac{R T_b^2}{\Delta \bar{H}} (1-x)
 \end{aligned}$$

where  $x$  is the mole fraction of solutes.

- We can also derive the above result from the chemical potential, where we get to the first to the second equation below because (standard) chemical potentials are equal at equilibrium.

$$\begin{aligned}
 \mu_i^\circ(T) + RT \ln x_1 &= \mu_g^\circ(T) + RT \ln \frac{P}{P_0} \\
 RT \ln x_1 &= RT \ln \frac{P}{P_0} + [\mu_g^\circ(T) - \mu_i^\circ(T)] \\
 &= RT \ln \frac{P}{P_0} + [\Delta \bar{H}_{\text{vap}} - T \Delta \bar{S}_{\text{vap}}] \\
 &= RT \ln \frac{P}{P_0} + [\Delta \bar{H}_{\text{vap}} - T_b \Delta \bar{S}_{\text{vap}} + (T_b - T) \Delta \bar{S}_{\text{vap}}] \\
 &= RT \ln \frac{P}{P_0} + \Delta T_b \cdot \frac{\Delta \bar{H}_{\text{vap}}}{T_b} \\
 \Delta T_b &= -\frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} \ln x_1 \\
 &= -\frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} \ln(1 - x_2) \\
 &\approx \frac{R T_b^2}{\Delta \bar{H}_{\text{vap}}} x_2
 \end{aligned}$$

- **Freezing point depression:** The decrease in the normal melting point of a mixture due to vapor pressure lowering.

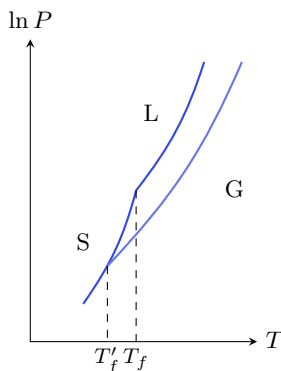


Figure 8.2: Freezing point depression.

- We know that  $\mu_g^\circ(T_f) = \mu_l^\circ(T_f)$ . Thus,

$$\begin{aligned}
 \mu_g^\circ(T) &= \mu_l^\circ(T) + RT \ln x_i \\
 RT \ln x_i &= \mu_g^\circ(T) - \mu_l^\circ(T) \\
 &= \Delta \bar{H}_{\text{fus}}(T) - T \Delta \bar{S}_{\text{fus}} \\
 &= (T_f - T) \Delta \bar{S}_{\text{fus}} \\
 &= (T_f - T) \frac{\Delta \bar{H}_{\text{fus}}}{T_f} \\
 &= -\Delta T_f \cdot \frac{\Delta \bar{H}_{\text{fus}}}{T_f} \\
 \Delta T_f &= -\frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} \ln x_1 \\
 &\approx \frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} x_2
 \end{aligned}$$

- The final result should be

$$\Delta T_f = -\frac{RT_f^2}{\Delta \bar{H}_{\text{fus}}} x_2$$

- The freezing point of water as more and more salt is added.

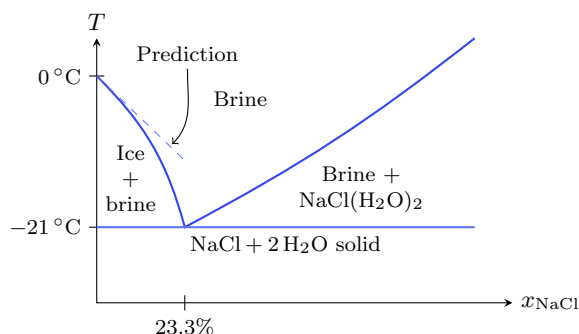


Figure 8.3: Freezing point vs. solute concentration.

- Osmotic pressure.

- Imagine a U-tube with a filter at the bottom that is porous to the solvent but nonporous to the solute.
- We know from Gen Chem that there will be excess pressure on the side with the impurities.
- Let  $\pi = \rho gh$  be the extra pressure where  $h$  is the height difference between the two sides and  $\rho$  is the density of the solvent.

$$\begin{aligned}
 \mu_l^\circ &= \mu_l = \mu_l^\circ + RT \ln x_1 + \pi \bar{V} \\
 0 &= RT \ln x_1 + \pi \bar{V} \\
 \pi &= \frac{RT}{\bar{V}} x_2
 \end{aligned}$$

- Ocean salinity is about 1 M, so  $\pi = 24$  atm. That means that in the tube, the right hand side will rise about as much as the Sears tower. Thus, the minimum amount of pressure/work you need is the height of the Sears tower minus 24 atm. Still, this is far more efficient than distillation.

## 8.2 Nonideal Solutions

- 3/2:
- When solutions are not ideal, we see deviations from Raoult's Law (Figure 7.1).
    - However, all solutions follow Raoult's Law when they are nearly pure.
    - When the actual partial pressure is higher, that means the substance would rather be in the vapor phase. When the actual partial pressure is lower, that means there is a favorable interaction between particles (they'd rather be in the dissolved state).

- Henry's Law:** Gives the tangent to the vapor pressure vs. mole percent graph at  $x_1 = 0$ . *Given by*

$$P_1 = k_H x_1$$

as  $x_1 \rightarrow 0$ .

- We know that  $A(g) \rightarrow A(\text{solv})$ .
  - At equilibrium  $\Delta \overline{G} = 0 = \Delta \overline{G}_{\text{solv}} + RT \ln x/P$ .
  - Thus,

$$P = x e^{\Delta \overline{G}_{\text{solv}}/RT}$$

- $x$  is the mixing entropy,  $P$  is the gas phase entropy.
- Microscopic enthalpy and entropy of solvation contribute to Henry's law, in addition to mixing entropy.
  - Larger  $k_H$  means less soluble.
- Temperature dependence.

$$k_{H,cp} = k_{H,cp}^{\Theta} \exp \left[ -C \cdot \left( \frac{1}{T} - \frac{1}{T^{\Theta}} \right) \right]$$

- $\Theta$  indicates reference temperature.
- It follows that as  $T$  increases,  $k_H$  increases.
  - For example,  $\text{O}_2$  is less soluble in water at higher temperatures.
  - This is consistent with solvation being an exothermic process.
- The activity and activity coefficient of a solute. Using Raoult's law as the reference for fully miscible substances.
  - We have for an ideal solution that  $\mu_i = \mu_i^* + RT \ln x_i$  and for an ideal gas that  $\mu_i = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$ .
  - These two equations together imply Raoult's law.
  - Now we want to keep the nice form of the above equations even with nonideality, so we do something similar to defining fugacity by defining the **activity**.
  - $a_i \rightarrow x_i$  as  $x_i \rightarrow 1$ .
  - As  $x_i \rightarrow 0$ , we have that

$$\begin{aligned} \mu_i^* + RT \ln a_i &= \mu_i^* + RT \ln \frac{P_i}{P_i^*} \\ &= \mu_i^* + RT \ln \frac{k_H}{P_i^*} x_i \end{aligned}$$

i.e.,  $a_i \rightarrow k_H x_i / P_i^*$ .

- As a substance becomes less active, it becomes more reactive.
- Activity:** A measure of the nonideality of solutions. *Denoted by  $a_i$ . Given by*

$$\mu_i = \mu_i^* + RT \ln a_i$$

- **Activity coefficient:** The following ratio. Denoted by  $\gamma$ . Given by

$$\gamma = \frac{a_i}{x_i}$$

- Example: Carbon disulfide/dimethoxymethane.

$x_{\text{CS}_2}$	$P_{\text{CS}_2}$ (torr)	$P_{\text{CH}_2(\text{OMe})_2}$ (torr)
0	0	587
0.1	109	529
1	514	0

Table 8.1: Pressure data for  $\text{CS}_2$  and  $\text{CH}_2(\text{OMe})_2$ .

- At  $x_{\text{CS}_2} = 0.1$ , we have that  $a_{\text{CS}_2} = 109/514$ .
- As  $x \rightarrow 0$ ,  $k_{H,\text{CS}_2} = 1130$  torr so  $a_{\text{CS}_2} = \frac{1130}{514} x_{\text{CS}_2}$ .
- See McQuarrie and Simon (1997) for using Henry's law as the reference state.
- Nonideality above the Raoult's law diagonal: More "active" than the ideal mixture.
- Nonideality below the Raoult's law diagonal: Less active than at low concentration.

### 8.3 Quantifying Deviations from Raoult's Law

- 3/4: • **Gibbs-Duhem relation:** A relation tying together the partial pressure of one substance to another, regardless of ideality/nonideality.

- We begin with

$$dG = \sum \mu_i dn_i + \sum n_i d\mu_i$$

at constant temperature and pressure.

- We also know from an earlier class that

$$G = \sum \mu_i n_i$$

- Differentiating the above, we get

$$dG = \sum \mu_i dn_i + \sum n_i d\mu_i$$

- It follows by setting the above two equations equal to each other that

$$\sum n_i d\mu_i = 0$$

- We can apply the Gibbs-Duhem relation to our expression for the chemical potential in terms of the activity coefficient.
- From last time,

$$\begin{aligned}\mu_i &= \mu_i^* + RT \ln(\gamma_i x_i) \\ d\mu_i &= RT d(\ln \gamma_i + \ln x_i)\end{aligned}$$

- It follows that

$$\begin{aligned}
 0 &= n_1 d\mu_1 + n_2 d\mu_2 \\
 &= \frac{1}{n_1 + n_2} (n_1 d\mu_1 + n_2 d\mu_2) \\
 &= \frac{n_1}{n_1 + n_2} RT d(\ln \gamma_1 + \ln x_1) + \frac{n_2}{n_1 + n_2} RT d(\ln \gamma_2 + \ln x_2) \\
 &= RT(x_1 d \ln x_1 + x_2 d \ln x_2 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2) \\
 &= dx_1 + dx_2 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 \\
 &= dx_1 - dx_1 + x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 \\
 &= x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2
 \end{aligned}$$

- Takeaway: If we know the activity coefficient for one component across the whole range, we can find the activity coefficient for the other component.
- In other words, knowing the chemical potential for one component gives us the chemical potential for the other.

- Relating  $P_1, P_2$  with the Gibbs-Duhem relation.

- We assume that we are in phase equilibrium. Thus, the chemical potential of the gas phase equals the chemical potential of the solution. In an equation,

$$\mu_1^* + RT \ln \frac{P_1}{P_1^*} = \mu_1 + RT \ln a_1$$

- Thus, applying the Gibbs-Duhem relation,

$$\begin{aligned}
 0 &= x_1 d \ln P_1 + x_2 d \ln P_2 \\
 &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 + x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2 \\
 &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} - x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}
 \end{aligned}$$

- Takeaway: The slopes of the curves on a pressure-concentration diagram are related, regardless of ideality/nonideality.

- **Margules equation:** An expansion to capture the experimental  $P(x)$  deviation from Raoult's law.

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \dots}$$

- An analytical form that gives us a good representation of experimentally-measured vapor pressures.
- Important features: Follows Henry's law at low concentrations of solute and Raoult's Law at high concentrations of solute.

- Margules equation covers Raoult's law and Henry's law.

- We have by the product rule of derivatives that

$$\frac{dP_1}{dx_1} = P_1^* \left[ e^{\alpha x_2^2 + \beta x_2^3 + \dots} + x_1 (-2\alpha x_2 - 3\beta x_2^2 - \dots) e^{\alpha x_2^2 + \beta x_2^3 + \dots} \right]$$

- As  $x_1 \rightarrow 1$ ,  $dP_1/dx_1 \rightarrow P_1^*$ . This can be seen because the above expression can be rewritten

$$\frac{dP_1}{dx_1} = P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \dots} [1 - 2\alpha x_1 x_2 - 3\beta x_1 x_2^2 - \dots]$$

- Implication: We recover Raoult's law as  $x_1 \rightarrow 1$ .
- Additionally, this explains why there is no linear terms in the exponent: If there were, one of the terms in the sum on the right-hand side above wouldn't go to zero as  $x_1 \rightarrow 1$ , meaning that  $dP_1/dx_1$  would not go to  $P_1^*$ .
- Recovering Henry's law as  $x_1 \rightarrow 0$ : As  $x_1 \rightarrow 0$ ,  $P_1 \rightarrow k_H x_1 = P_1^* e^{\alpha + \beta + \dots} \cdot x_1$ .
- Margules equation parameters fitted for  $P_1$  provide a related equation for  $P_2$  based on Gibbs-Duhem (Problem 24-33).
- To two terms, the Margules equation tells us that

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

- As we showed earlier, the Gibbs-Duhem equation implies that

$$x_1 \frac{\partial \ln P_1}{\partial x_1} = x_2 \frac{\partial \ln P_2}{\partial x_2}$$

- Thus, since  $x_2 = 1 - x_1$ ,

$$\begin{aligned} x_1 \frac{\partial \ln P_1}{\partial x_1} &= x_1 \frac{\partial}{\partial x_1} (\ln x_1 + \alpha x_2^2 + \beta x_2^3 + \text{terms not involving } x_1) \\ &= x_1 \left[ \frac{1}{x_1} + (-2\alpha x_2) + (-3\beta x_2^2) \right] \\ &= 1 + x_2(-2\alpha x_1 - 3\beta x_1 x_2) \\ &= 1 + x_2(-2\alpha x_1 - 3\beta x_1(1 - x_1)) \\ &= 1 + x_2(-2\alpha x_1 - 3\beta(x_1 - x_1^2)) \\ &= 1 + x_2[-(2\alpha + 3\beta)x_1 + 3\beta x_1^2] \end{aligned}$$

- Now let

$$P_2 = x_2 P_2^* e^{a x_1^2 + b x_1^3}$$

- It follows as before that

$$x_2 \frac{\partial \ln P_2}{\partial x_2} = 1 + x_2(-2a x_1 - 3b x_1^2)$$

- Direct comparison reveals that

$$\begin{aligned} -2a &= -(2\alpha + 3\beta) & -3b &= 3\beta \\ a &= \alpha + \frac{3}{2}\beta & b &= -\beta \end{aligned}$$

so

$$P_2 = x_2 P_2^* e^{(\alpha + \frac{3}{2}\beta)x_1^2 - \beta x_1^3}$$

- **Regular solution:** A solution for which only  $\alpha \neq 0$  and every other Margules parameter is zero.

- In this case,

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

- This means that the Raoult's activity of the two solutions is entirely symmetric over the range of compositions.
- This does not necessarily imply that the vapor pressures vary in the same way.
- Mixing Gibbs free energy for a regular solution (24-5).

– We have

$$\begin{aligned}
 \frac{\Delta G_{\text{mix}}}{RT} &= \underbrace{n_1 \mu_1^{\text{sol}} + n_2 \mu_2^{\text{sol}}}_{\text{mixture}} - \underbrace{(n_1 \mu_1^* + n_2 \mu_2^*)}_{\text{pure}} \\
 &= n_1 \ln \frac{P_1}{P_1^*} + n_2 \ln \frac{P_2}{P_2^*} \\
 &= n_1 \ln x_1 + n_2 \alpha x_2^2 + n_2 \ln x_2 + n_2 \alpha x_1^2 \\
 \frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2^2 + \alpha x_2 x_1^2 \\
 &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2 (x_1 + x_2) \\
 \frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} &= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2
 \end{aligned}$$

- The left two terms above represent the entropy of mixing (which does not depend on interaction).
- The right term above is the enthalpy/entropy of mixing which depends *only* on interaction.
- Thus,  $\alpha$  is the microscopic entropy of mixing for a regular solution.
- The upper critical solution temperature (UCST) (critical temperature above which the components of the mixture are miscible in all proportions).

– We have

$$\Delta \bar{G} = RT(x_1 \ln x_1 + x_2 \ln x_2) + \underbrace{RT\alpha x_1 x_2}_{\Omega}$$

- Graphing the above equation will help us determine what extent of mixing will be most energetically favorable.
  - In particular, if we graph the left two terms, that tells us the entropy of mixing, which will be greatest at  $x_1 = x_2$ .
  - Graphing the right term on the other hand yields a parabola.
  - As such, since  $x_1 \ln x_1 + x_2 \ln x_2$  has vertical slope at  $x_1 = 0, 1$  and the other term simply has some positive slope, entropy of mixing will always win at low concentrations of solutes, i.e., when you have a small enough concentration of solute in solvent, you will always observe mixing.
  - However, the overall graph may have minima on the two sides, indicating that forming a fully mixed solution is not energetically favorable, but it is most favorable to separate into substance 1 with a bit of substance 2 and vice versa (think oil and water).
  - At high temperatures, however, this effect goes away and mixing always becomes the most favorable state.
- The temperature at which the overall graph only has one minimum for the first time is the UCST.

## 8.4 Office Hours (PGS)

- Can you go over the spontaneous expansion of an ideal gas from one isolated container to two? Is this an adiabatic process or an isothermal process? How can the gas cool down during the expansion if it ends up at the same final temperature?
  - An isoenthalpic expansion? Only as long as we can neglect the back pressure of the far wall. In this moment,

$$\begin{aligned}
 0 &= \Delta H \\
 &= \Delta U + \Delta KE + \Delta(PV)
 \end{aligned}$$



- The gas shooting out is expanding and picking up a lot of kinetic energy, but we need to conserve enthalpy all together, so that kinetic energy comes from vibrational and spin states.
- After everything comes to equilibrium, though, the temperature is the same.
- It's irreversible, so that means that during the process, you do not have well-defined state variables.
- Note that no work is done even for the intermixing of two gases.
  - Any work done by one gas is canceled by the work on the other gas and no work comes out of the system; it's a pure entropy effect.
  - But work is being done by both gases; just equal and opposite?
- How does the Henry's law we learned relate to the one from Gen Chem (the amount of gas dissolved in solution is proportional to its partial pressure)?
  - The Henry's law of intro chem says that concentration vs. pressure will always be a straight line.
  - We know now that we see deviations at higher concentrations, and that Henry's law is just a good approximation at relatively low pressures.
- Demixing of solutions at lower temperatures?
  - The line connecting all of the two minima with peak at the UCMT is the **spinodal line**.

## 8.5 Chapter 24: Solutions I — Liquid-Liquid Solutions

From McQuarrie and Simon (1997).

- There exist positive and negative deviations from Raoult's Law (see Figure 8.4).

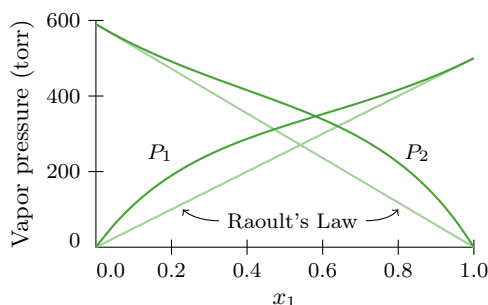


Figure 8.4: Positive deviations from Raoult's law ( $\text{CS}_2/\text{CH}_2(\text{OMe})_2$  at  $25^\circ\text{C}$ ).

- If 1 and 2 denote two substances that are being mixed, positive deviations occur when 1-2 interactions are more repulsive than either 1-1 or 2-2 interactions, and vice versa for negative deviations.
- If one component of a binary solution exhibits positive deviations from Raoult's law, so must the other component.
  - Follows from “Relating  $P_1, P_2$  with the Gibbs-Duhem relation” as in class.
- Molecular structure predicts deviations from Raoult's law.

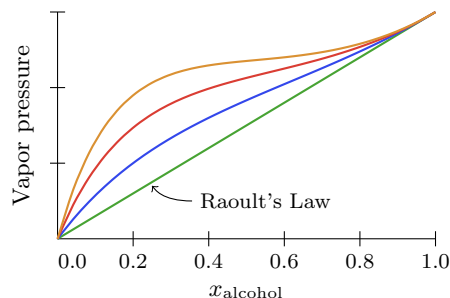


Figure 8.5: Vapor pressure of alcohol/water solutions.

- The blue line represents MeOH, the red line represents EtOH, and the orange line represents PrOH.
- Notice how as molecular structure gets further from that of H<sub>2</sub>O (the solvent), deviations become more exaggerated.
- McQuarrie and Simon (1997) discusses the limiting behavior of  $P_1$  in Figure 8.4, noting the Raoult's law limit as  $x_1 \rightarrow 1$  and introducing **Henry's law**.
- **Henry's law**: The partial pressure of a component in solution approaches the linear function  $k_{H,i}x_i$  as  $x_i \rightarrow 0$ .
- **Henry's law constant**: The constant  $k_{H,i}$  in the above definition.
- For an ideal solution,  $k_{H,i} = P_i^*$ , but this is not true in general (as illustrated by Figure 8.4).
- Example: Finding  $P_1^*$  and  $k_H$  from an equation for  $P_1$ .
  - Let  $P_1 = 180x_1e^{x_2^2 + \frac{1}{2}x_2^3}$ .
  - As  $x_1 \rightarrow 1$ ,  $x_2 \rightarrow 0$ , so  $P_1 \rightarrow 180x_1$ . Since this form should be the Raoult's law limit, we can read off  $P_1^* = 180$  torr.
  - As  $x_1 \rightarrow 0$ ,  $x_2 \rightarrow 1$ , so  $P_1 \rightarrow 180x_1e^{1 + \frac{1}{2}} = 180e^{3/2}x_1$ . Since this form should be the Henry's law limit, we can read off  $k_{H,1} = 180e^{3/2} = 807$  torr.

- McQuarrie and Simon (1997) derives

$$x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}$$

as in class.

- In a binary solution, if component 1 obeys Raoult's law as  $x_1 \rightarrow 1$ , then component 2 obeys Henry's law as  $x_2 \rightarrow 0$ .
  - Suppose component 1 satisfies  $P_1 \rightarrow x_1 P_1^*$  as  $x_1 \rightarrow 1$ . Then

$$\begin{aligned} x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} &= x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} \\ &= x_1 \frac{\partial}{\partial x_1} (\ln x_1 + \ln P_1^*) \\ &= 1 \\ \ln P_2 &= \int \frac{1}{x_2} dx_2 \\ &= \ln x_2 + C \\ P_2 &= k_H x_2 \end{aligned}$$

as desired.

- The vapor pressure curve of WLOG component 1 of a binary solution can often be represented empirically by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

- $\alpha, \beta$  reflect the extent of the nonideality of the solution in some manner because  $P_1 = x_1 P_1^*$  (ideal) for  $\alpha = \beta = 0$ .
- Furthermore, generalizing from the previous example,  $k_{H,1} = P_1^* e^{\alpha + \beta}$  and  $k_{H,2} = P_2^* e^{\alpha + \beta/2}$  (the latter equation will be derived presently).
- Deriving  $P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$  from  $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$  in an alternate manner to what was presented in class.

- We are given that  $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$  and that  $x_2 = 1 - x_1$ .
- It follows that the chemical potential of component 1 is

$$\begin{aligned}\mu_1 &= \mu_1^\circ + RT \ln P_1 \\ &= \mu_1^\circ + RT [\ln P_1^* + \ln x_1 + \alpha(1 - x_1)^2 + \beta(1 - x_1)^3]\end{aligned}$$

- It follows that the total differential of  $\mu_1(x_1)$  is

$$d\mu_1 = RT \left[ \frac{1}{x_1} - 2\alpha(1 - x_1) - 3\beta(1 - x_1)^2 \right] dx_1$$

- Thus, by the Gibbs-Duhem equation,

$$\begin{aligned}x_1 d\mu_1 + x_2 d\mu_2 &= 0 \\ d\mu_2 &= -\frac{x_1}{x_2} \cdot RT \left[ \frac{1}{x_1} - 2\alpha(1 - x_1) - 3\beta(1 - x_1)^2 \right] dx_1 \\ &= RT \left[ -\frac{1}{x_2} + 2\alpha x_1 + 3\beta x_1(1 - x_1) \right] dx_1\end{aligned}$$

- Substitute  $x_2 = 1 - x_1$  and integrate.

$$\begin{aligned}d\mu_2 &= RT \left[ \frac{1}{x_2} - 2\alpha(1 - x_2) - 3\beta x_2(1 - x_2) \right] dx_2 \\ \int_1^{x_2} d\mu_2 &= RT \int_1^{x_2} \left[ \frac{1}{x_2'} - 2\alpha(1 - x_2') - 3\beta x_2'(1 - x_2') \right] dx_2' \\ \mu_2(x_2) - \mu_2(1) &= RT \left[ \ln x_2 + \alpha(1 - x_2)^2 - \frac{3\beta}{2}(x_2^2 - 1) + \beta(x_2^3 - 1) \right] \\ \mu_2 - \mu_2^* &= RT \left[ \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2}x_1^2 - \beta x_1^3 \right]\end{aligned}$$

- Therefore, since

$$\mu_2 = \mu_2^\circ + RT \ln P_2 \qquad \mu_2^* = \mu_2^\circ + RT \ln P_2^*$$

we have that

$$\begin{aligned}\ln P_2 &= \ln P_2^* + \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2}x_1^2 - \beta x_1^3 \\ P_2 &= x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}\end{aligned}$$